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## IX.—ON THE DIASTATIC ACTION OF SALIVA.

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I.—*Influence of Acids, Alkalies, and Gastric Juice on the diastatic Action of Saliva.*

Human mixed saliva ordinarily possesses, when freshly secreted, an alkaline reaction. The saliva of the parotid gland, however, which contains the greater part of the diastatic ferment, has, according to Astaschewsky,[1] a very faint acid reaction, which gives place to an alkaline reaction when the mucous membrane of the mouth is strongly irritated. According to the same investigator, the maximum of the diastatic action of parotid saliva corresponds with the strongest acid reaction. It has usually been stated that a slight alteration of the reaction of saliva does not affect its diastatic action; thus years ago Jacubowitsch and Paschutin reported that the addition of caustic soda to distinct alkaline reaction did not hinder the action of the ferment, while, according to Schiff, the ferment was irredeemably destroyed by acids. On the other hand, Lehman,[2] Schiff, Ebstein and others agreed that the addition of small quanti-

[1] Centralblatt f. d. med. Wissensch. 1878, 15.

[2] See Maly in Hermann's Handbuch der Physiologie, Band 5, Theil 1, p. 33.

ties of acids was without influence on the conversion of starch into sugar. Again Jacubowitsch[1] reported the results of several experiments where the gastric juice of a dog was mixed with human saliva in such proportions that neutral, acid and alkaline solutions were obtained, and in all of these cases the action upon starch was the same; all three fluids furnished sugar, but in these experiments there was nothing to indicate the amounts of sugar formed. Watson[2] found as a result of experiment that by the addition of small quantities of acid the diastatic action of saliva was decidedly increased; thus he found that while 400 grains of plain saliva yielded 1.234 grains of glucose, the same amount of saliva, acidified by the addition of one drop of hydrochloric acid (sp. gr. 1.16), yielded 1.708 grains of glucose. From this he concludes that "saliva will be more active upon farinaceous bodies when mixed with the acid fluid of the stomach than it would otherwise be." Münk[3] found that diastase from saliva and pancreatic juice was hindered in its action by .2 per cent. hydrochloric acid, but would tolerate a relatively higher grade of alkalescence.

Naturally in experiments of this kind the concentration of the fluid has considerable influence on the action of the ferment. Thus Paschutin[4] remarks that if carefully neutralized saliva is diluted with water in various proportions, it will be found that a content of acid which, in the undiluted saliva, would cause a greater or less diminution of the diastatic action, will in more dilute samples actually aid in the diastatic process. That the ferment is not destroyed is manifested by the fact that after neutralization of the acid the action again goes on. Thus Maly,[5] basing his observations on these data, says the conversion of starch in the stomach will continue or not according to the quantity of the acid present and its proportion to the ferment present. Therefore, says Maly, the percentage of acid which absolutely hinders can be designated only for a definite mixture and not in a general sense. So Brücke[6] found, when he added to neutralized saliva an equal volume of very dilute hydrochloric acid (.2 per cent.), that the mixture no longer possessed the property of converting starch into sugar. If the mixture contained but one-half gram of hydrochloric acid or

[1] See Lehman's Zeochemie, p. 22.
[2] Jour. Chem. Soc. 1879, 543.
[3] See abstract in Jahresbericht u. d. Fortschritte d. Thierchemie für 1876, 271.
[4] Archiv. f. Anat. u. Physiol. 1871, 305.
[5] Hermann's Handbuch d. Physiologie, 5 B. 1 Theil, 34.
[6] Sitzungsber. d. Wiener. Acad. 3 Abth. 1872.

less to the litre, the fluid then was capable of changing the starch into sugar. Hammastern[1] likewise found that in the majority of cases a content of .05–.25 per cent. of hydrochloric acid entirely stopped the diastatic action.

It is thus very evident that there is a great diversity of opinion in regard to the influence of acids and alkalies on the diastatic action of saliva, and likewise as to the effect of acid of the strength of the gastric juice when the two fluids are mixed in the stomach during normal digestion. It is quite natural that the diastatic action of saliva should vary somewhat at different times and under different circumstances; thus variations of temperature, concentration of fluid, length of time of digestion, etc., probably exert some modifying influence, particularly as recent investigation has shown the presence of several carbohydrate products as a result of salivary digestion. Therefore the different experiments about to be described were carried on in series and in such a manner as to obtain uniformity in the various steps of the process, while at the same time one experiment of each series serves as a control, by means of which the diastatic action of the acid or alkaline saliva can be compared with the diastatic action of normal saliva of the same collecting, thus enabling us to accurately measure the influence of the acid or alkali on the diastatic action.

Again it is an important point to ascertain, if possible, the effect of the acid and alkaline fluids of the stomach and intestines on the action of saliva, and as the acid gastric juice is present in the stomach during digestion in great excess over the saliva, we deemed it more in accord with the conditions as they exist in the body to have the saliva present in these experiments in the proportion of one-fourth of the whole mixture. Thus in each digestion 100 cc. of fluid were used, of which 25 cc. were filtered mixed saliva.

The method employed in conducting the digestions was as follows: 1 gram of starch was made into a paste by boiling with 25 cc. of water, then, when cold, 50 cc. of the diluted acid or alkali were added, and finally 25 cc. of filtered human saliva; while, in the control experiment, 50 cc. of water were added in place of the acid or alkali, so that the dilution was the same in each case. The mixtures were then placed in a water-bath at 38-40°C. for a definite period, usually 45 minutes, with occasional stirring. At the end of

[1] Jahresber. d. ges. Med. 1871, 1.

this time the fluid was carefully neutralized and then quickly boiled to destroy the ferment. The mixture was then diluted with water to 500 cc., and, when thoroughly mixed, 50 cc. of this fluid were filtered from the unchanged starch, and in this one-tenth the sugar and other reducing substances were determined gravimetrically according to the method which has been so carefully elaborated by Maercker [1] and others.

The Fehling's solution was prepared by dissolving 34.632 grams of pure cupric sulphate in 1 litre of water. A second solution was made by dissolving 63 grams of sodium hydroxide and 173 grams of recrystallized potassium and sodium tartrate likewise in 1 litre of water. When the sugar was to be determined, 25 cc. of each solution were placed in a small beaker, and then 50 cc. of the diluted and filtered digestive mixture were added, making thereby 100 cc. of fluid. The beaker was then placed in a bath of boiling water for 20 minutes, after which the precipitate of cuprous oxide was filtered off and washed with 300 cc. of boiling water. After drying, the precipitate was ignited in a current of hydrogen and weighed as metallic copper, from which the amount of reducing substance, calculated as dextrose, was ascertained by the use of the tables devised by Maercker, who determined by means of pure dextrose the reduction equivalent of different quantities of sugar under the conditions above described.

### First Series of Experiments.[2]

I. 1 gram starch in 25 cc. $H_2O$+50 cc. $H_2O$+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0864 gram Cu. Entire yield of dextrose, .4685 gram.

II. 1 gram starch in 25 cc. $H_2O$+50 cc. .01 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .09305 gram Cu. Entire yield of dextrose, .5155 gram.

III. 1 gram starch in 25 cc. $H_2O$+50 cc. .05 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0797 gram Cu. Entire yield of dextrose, .422 gram.

IV. 1 gram starch in 25 cc. $H_2O$+50 cc. .1 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0081 gram Cu. Entire yield of dextrose, .0429 gram.

[1] Die Landwirthschaftliche Versuchs-Stationen, **25**, 115-116.

[2] The saliva used in each series of experiments was collected at one time, thoroughly mixed, and then filtered.

### Second Series of Experiments.

I. 1 gram starch in 25 cc. $H_2O$+50 cc. $H_2O$+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0892 gram Cu. Entire yield of dextrose, .4835 gram.

II. 1 gram starch in 25 cc. $H_2O$+50 cc. .01 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .1054 gram Cu. Entire yield of dextrose, .5357 gram.

III. 1 gram starch in 25 cc. $H_2O$+50 cc. .05 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0477 gram Cu. Entire yield of dextrose, .2655 gram.

IV. 1 gram starch in 25 cc. $H_2O$+50 cc. .1 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .01135 gram Cu. Entire yield of dextrose, .0578 gram.

### Third Series of Experiments.

I. 1 gram starch in 25 cc. $H_2O$+50 cc. $H_2O$+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0898 gram Cu. Entire yield of dextrose, .487 gram.

II. 1 gram starch in 25 cc. $H_2O$+50 cc. .01 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0926 gram Cu. Entire yield of dextrose, .5085 gram.

III. 1 gram starch in 25 cc. $H_2O$+50 cc. .05 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0671 gram Cu. Entire yield of dextrose, .3455 gram.

IV. 1 gram starch in 25 cc. $H_2O$+50 cc. .1 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .007 gram Cu. Entire yield of dextrose, .036 gram.

### Fourth Series of Experiments.

I. 1 gram starch in 25 cc. $H_2O$+50 cc. $H_2O$+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0833 gram Cu. Entire yield of dextrose, .4465 gram.

II. 1 gram starch in 25 cc. $H_2O$+50 cc. .01 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0921 gram Cu. Entire yield of dextrose, .506 gram.

III. 1 gram starch in 25 cc. $H_2O$+50 cc. .05 per cent. $Na_2CO_3$+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0761 gram Cu. Entire yield of dextrose, .399 gram.

IV. 1 gram starch in 25 cc. $H_2O$+50 cc. .1 per cent. $Na_2CO_3$+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0735 gram Cu. Entire yield of dextrose, .3815 gram.

V. 1 gram starch in 25 cc. $H_2O$+50 cc. .3 per cent. $Na_2CO_3$+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0791 gram Cu. Entire yield of dextrose, .419 gram.

FIFTH SERIES OF EXPERIMENTS.

I. 1 gram starch in 25 cc. $H_2O$+50 cc. $H_2O$+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0873 gram Cu. Entire yield of dextrose, .4735 gram.

II. 1 gram starch in 25 cc. $H_2O$+50 cc. .01 per cent. $Na_2CO_3$+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .083 gram Cu. Entire yield of dextrose, .4445 gram.

III. 1 gram starch in 25 cc. $H_2O$+50 cc. .05 per cent. $Na_2CO_3$+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0789 gram Cu. Entire yield of dextrose, .418 gram.

IV. 1 gram starch in 25 cc. $H_2O$+50 cc. .1 per cent. $Na_2CO_3$+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0742 gram Cu. Entire yield of dextrose, .3853 gram.

V. 1 gram starch in 25 cc. $H_2O$+50 cc. .3 per cent. $Na_2CO_3$+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0602 gram Cu. Entire yield of dextrose, .3065 gram.

SIXTH SERIES OF EXPERIMENTS.

I. 1 gram starch in 25 cc. $H_2O$+50 cc. $H_2O$+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0808 gram Cu. Entire yield of dextrose, .428 gram.

II. 1 gram starch in 25 cc. $H_2O$+50 cc. .05 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0742 gram Cu. Entire yield of dextrose, .3855 gram.

III. 1 gram starch in 25 cc. $H_2O$+50 cc. .1 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced an unweighable trace of Cu.

IV. 1 gram starch in 25 cc. $H_2O$+50 cc. of an active gastric juice[1] containing .05 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0991 gram Cu. Entire yield of dextrose, .5615 gram.

V. 1 gram starch in 25 cc. $H_2O$+50 cc. of an active gastric juice containing .1 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. failed to show any reducing power whatever.

SEVENTH SERIES OF EXPERIMENTS.

I. 1 gram starch in 25 cc. $H_2O$+50 cc. $H_2O$+25 cc. saliva, 38–40°C. for 65 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .079 gram Cu. Entire yield of dextrose, .4185 gram.

II. 25 cc. saliva + 50 cc. .2 per cent. HCl. Warmed at 38–40°C. for 2 hours; solution then neutralized, 1 gram starch in 25 cc. $H_2O$ added to the neutralized fluid, and the mixture warmed at 38–40°C. for 45 min., boiled and

[1]The gastric juice used in the different experiments was prepared by adding to 100 cc. hydrochloric acid of the strength specified, 5 cc. of a glycerin extract of pepsin, made from the cardiac mucosa of a pig's stomach.

diluted to 500 cc., 50 cc. sol. reduced .0219 gram Cu. Entire yield of dextrose, .1112 gram.

III. 25 cc. saliva + 50 cc. of an active gastric juice containing .2 per cent. HCl. Warmed at 38–40°C. for two hours; solution neutralized, 1 gram starch in 25 cc. $H_2O$ added, and the mixture kept at 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. gave only a very slight trace of $Cu_2O$.

### Eighth Series of Experiments.

I. 1 gram starch in 25 cc. $H_2O$+50 cc. $H_2O$+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0982 gram Cu. Entire yield of dextrose, .5565 gram.

II. 1 gram starch in 25 cc. $H_2O$+50 cc. .1 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0048 gram Cu. Entire yield of dextrose, .0244 gram.

III. 1 gram starch in 25 cc. $H_2O$+50 cc. .01 per cent. $Na_2CO_3$+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0965 gram Cu. Entire yield of dextrose, .545 gram.

IV. 1 gram starch in 25 cc. $H_2O$+50 cc. .6 per cent. $Na_2CO_3$+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0808 gram Cu. Entire yield of dextrose, .428 gram.

V. 1 gram starch in 25 cc. $H_2O$+50 cc. gastric juice containing .1 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced only a very slight trace of Cu.

VI. 25 cc. saliva + 50 cc. .2 per cent. HCl, 38–40°C. for 2 hours. Solution neutralized, and 1 gram starch in 25 cc. $H_2O$ added, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0361 gram Cu. Entire yield of dextrose, .1982 gram.

VII. 25 cc. saliva + 50 cc. gastric juice containing .2 per cent. HCl, 38–40°C. for 2 hours. Solution neutralized, and 1 gram starch in 25 cc. $H_2O$ added, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. yielded only a very slight trace of $Cu_2O$.

### Ninth Series of Experiments.

I. 1 gram starch in 25 cc. $H_2O$+50 cc. $H_2O$+25 cc. saliva, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0776 gram Cu. Entire yield of dextrose, .407 gram.

II. 1 gram starch in 25 cc. $H_2O$+50 cc. .1 per cent. $Na_2CO_3$+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0762 gram Cu. Entire yield of dextrose, .3995 gram.

III. 1 gram starch in 25 cc. $H_2O$+50 cc. .6 per cent. $Na_2CO_3$+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0765 gram Cu. Entire yield of dextrose, .401 gram.

IV. 1 gram starch in 25 cc. $H_2O$+50 cc. gastric juice containing .05 per cent. HCl+25 cc. saliva, 38–40°C. for 45 min., neutralized, boiled and diluted to 500 cc., 50 cc. sol. reduced .0981 gram Cu. Entire yield of dextrose, .556 gram.

V. 25 cc. saliva + 50 cc. .2 per cent. HCl, 38–40°C. for 2 hours. Solution neutralized, and 1 gram starch in 25 cc. $H_2O$ added, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. reduced .0129 gram Cu. Entire yield of dextrose, .066 gram.

VI. 25 cc. saliva + 50 cc. gastric juice containing .2 per cent. HCl, 38–40°C. for 2 hours. Solution neutralized, and 1 gram starch in 25 cc. $H_2O$ added, 38–40°C. for 45 min., boiled and diluted to 500 cc., 50 cc. sol. showed no trace of sugar.

Arranging these results in tabular form we have Table I., in which the figures represent the entire amount of dextrose expressed in grams obtained from one gram of starch by the action of 25 cc. of saliva. The percentages represent the amount of acid or alkali in the entire fluid, viz. in the 100 cc.

TABLE I.

| | 1st Series. | 2d Series. | 3d Series. | 4th Series. | 5th Series. | 6th Series. | 7th Series. | 8th Series. | 9th Series. |
|---|---|---|---|---|---|---|---|---|---|
| $H_2O$..... | .4685 | .4835 | .4870 | .4465 | .4735 | .4280 | .4185 | .5565 | .4070 |
| .005 per cent. HCl.... | .5155 | .5357 | .5085 | .5060 | .. | .. | .. | .. | .. |
| .025 per cent. HCl.... | .4220 | .2655 | .3455 | .. | .. | .3855 | .. | .. | .. |
| .050 per cent. HCl.... | .0429 | .0578 | .0360 | .. | .. | 0 | .. | .0244 | .. |
| .005 per cent. $Na_2CO_3$ | .. | .. | .. | .. | .4445 | .. | .. | .5450 | .. |
| .025 per cent. $Na_2CO_3$ | .. | .. | .. | .3990 | .4180 | .. | .. | .. | .. |
| .050 per cent. $Na_2CO_3$ | .. | .. | .. | .3815 | .3853 | .. | .. | .. | .3995 |
| .150 per cent. $Na_2CO_3$ | .. | .. | .. | .4190 | .3065 | .. | .. | .. | .. |
| .300 per cent. $Na_2CO_3$ | .. | .. | .. | .. | .. | .. | .. | .4280 | .4010 |
| .025 per cent. HCl gastric juice..... | .. | .. | .. | .. | .. | .5615 | .. | .. | .5560 |
| .050 per cent. HCl gastric juice..... | .. | .. | .. | .. | .. | 0 | .. | 0 | .. |
| Saliva warmed with .2 per cent. HCl for 2 hours, then neutralized and used..... | .. | .. | .. | .. | .. | .. | .1112 | .1982 | .0660 |
| Saliva digested with .2 per cent. HCl gastric juice for 2 hours, then neutralized and used | .. | .. | .. | .. | .. | . | 0 | 0 | 0 |

In order to have the rate of increase or decrease in the diastatic action of the saliva more apparent under the various conditions, Table II. has been devised, showing the ratio of each determination to its control, making the latter 100.

TABLE II.

| | 1st Series | 2d Series | 3d Series | 4th Series | 5th Series | 6th Series | 7th Series | 8th Series | 9th Series | Mean Ratio |
|---|---|---|---|---|---|---|---|---|---|---|
| $H_2O$..... | 100. | 100. | 100. | 100. | 100. | 100. | 100. | 100. | 100. | 100. |
| .005 per cent. HCl..... | 110.02 | 110.79 | 104.41 | 113.32 | .. | .. | .. | .. | .. | 109.63 |
| .025 per cent. HCl..... | 90.07 | 54.91 | 70.94 | .. | .. | 90.07 | .. | .. | .. | 76.49 |
| .050 per cent. HCl ..... | 9.15 | 11.95 | 7.39 | .. | .. | 0 | .. | 4.38 | .. | 8.21 |
| .005 per cent. $Na_2CO_3$.... | .. | .. | .. | .. | 93.87 | .. | .. | 97.93 | .. | 95.90 |
| .025 per cent. $Na_2CO_3$.... | .. | .. | .. | 89.36 | 88.27 | .. | .. | .. | .. | 88.81 |
| .050 per cent. $Na_2CO_3$.... | .. | .. | .. | 85.44 | 81.37 | .. | .. | .. | 98.15 | 88.32 |
| .150 per cent. $Na_2CO_3$.... | .. | .. | .. | 93.84 | 64.73 | .. | .. | .. | .. | 79.28 |
| .300 per cent. $Na_2CO_3$.... | .. | .. | .. | .. | .. | .. | .. | 76.90 | 98.52 | 87.71 |
| .025 per cent. HCl gastric juice..... | .. | .. | .. | .. | .. | 131.19 | .. | .. | 136.60 | 133.89 |
| .050 per cent. HCl gastric juice..... | .. | .. | .. | .. | .. | 0 | .. | 0 | .. | 0 |
| Saliva warmed with .2 per cent. HCl for 2 hours, then neutralized and used..... | .. | .. | .. | .. | .. | .. | 26.57 | 35.61 | 16.21 | 26.13 |
| Saliva digested with .2 per cent. HCl gastric juice for 2 hours, then neutralized and used..... | .. | .. | .. | .. | .. | .. | 0 | 0 | 0 | 0 |

By a glance at the above results we notice first that the presence of acid to the extent of .005 per cent. decidedly increases the diastatic action, while an increase of acid beyond this percentage diminishes the diastatic action of the saliva to a very marked degree. Further experiments conducted with still stronger solutions of acid (.1 per cent., .2 per cent. and .4 per cent. HCl), showed the action to be wholly stopped. The increase in the amount of sugar formed in a faintly acid solution (.005 per cent.) would tend to corroborate the statement of Astaschewsky[1] that the maximum of the diastatic action of parotid saliva corresponds with the strongest acid reaction. The next most noticeable feature is the effect produced by the addition of sodium carbonate, the diastatic action being somewhat diminished, though not materially further affected by an increased percentage of the alkali. The fluids of the intestinal canal are distinctly alkaline, the pancreatic juice, which is most actively concerned in the chemical changes occurring in the intestines, is likewise strongly alkaline; containing presumably an amount of alkali corresponding to .3 per cent. of sodium carbonate. The above experiments then show that an alkaline solution of the strength most favorable for the digestive action of trypsin does not impede to any great extent the action of the ptyalin of pancreatic juice, while any salivary ptyalin which may have survived the action of the gastric juice would again be active

[1] Centralblatt f. d. med. Wissensch. 1878, 15.

under the conditions of the intestinal canal. Just here it may be well to notice the probable effect of a mixture of saliva and gastric juice. Most authorities agree in the statement that the action of saliva is arrested in the stomach by the acidity of the gastric juice, but that when the acid of the chyme is neutralized by the fluids of the intestinal canal the diastatic action of the saliva again goes on. Watson, however, as already quoted, states that saliva will be more active on starchy matters when mixed with the acid fluid of the stomach than it would otherwise be. Our experiments show conclusively that long before the strength of acid approximates to the acid of gastric juice, the diastatic action of the saliva is entirely stopped. Again Maly[1] says that "the salivary ferment is not altered or digested in the stomach, for Connheim found that after 24 hours digestion in an active gastric juice, its diastatic action was again apparent on neutralization."

Our experiments, however, would seem to indicate the incorrectness of the above statement. The experiments, as the preceding results show, were first tried by mixing together gastric juice, starch and saliva, and warming this mixture at the body temperature. When the percentage of hydrochloric acid was .025 there was a notable increase in the diastatic action, for which it is hard to find a suitable explanation. The gastric juice itself, however, appeared to possess to a very slight degree the power of converting starch into sugar, probably in virtue of the presence of a trace of the pyloric ferment in the glycerin, but experiment showed that this could not have played a very important part in the increased formation of sugar.[2] With .05 per cent. hydrochloric acid gastric juice the action was wholly stopped. By previously digesting saliva with an active gastric juice for two hours at 40° C. the diastatic action of the saliva appeared to be wholly destroyed, or at least nearly so. Repeated experiments tried in the manner already described, but without diluting the fluid after digestion, showed that in the concentrated fluid there was a slight reducing action, but the amount of sugar formed must have been exceedingly small. The low diastatic power of the saliva treated with .2 per cent. HCl for two hours was probably dependent in part on the neutral condition of the fluid, and possibly on the presence of the neutral salt

[1] In Herrmann's Handbuch d. Physiologie, Band 5, Theil 1, p. 113.

[2] Experiments now in progress in this laboratory point to a probable explanation of this fact.

formed by neutralization, but it seems more than probable that a part of the ferment was destroyed by the acid.

That the ferment ptyalin should be digested and thus destroyed by the acid solution of pepsin does not seem at all impossible. It is well known that the pancreatic trypsin is digested by gastric juice, and there is no evidence that the salivary ptyalin is less susceptible of change under like circumstances.

Thus it would seem from our experiments that the diastatic ferment of saliva is not only hindered in its action by the acidity of the gastric juice, but that it is, in part at least, destroyed, and thus debarred from any further part in the conversion of starch into sugar.

II.—*Products of Salivary Digestion.*

In order to study in detail the different products which result from the action of saliva on starch, several digestions were made with large quantities of material, the results of which were exceedingly satisfactory. 40 grams of starch made into a paste by boiling with 600 cc. water were digested with 200 cc. of filtered saliva for 15 hours at 40° C. The mixture was then evaporated to dryness on a water-bath, and the semi-dry residue treated with 700 cc. of 95 per cent. alcohol, which was allowed to remain in contact with it for 24 hours. The residue, which was mainly composed of unaltered starch, contained a body of strong reducing power and apparently dextro-rotary.

To the alcoholic solution 300 cc. of ether were added, and the mixture allowed to stand several days, at the end of which time quite a heavy gummy precipitate had settled out. The supernatant fluid was poured off and treated again with ether. After several days a second gummy precipitate formed, and by again adding a large quantity of ether to the solution a third colorless and gummy precipitate was obtained. By treating this filtrate with ether another precipitate gradually settled out, which, on standing a few days, was found to be composed wholly of small, white needle-like crystals.

This crystalline precipitate was washed with large quantities of ether and then dried over oil of vitriol, and finally at 112°C. until a constant weight was obtained. The dried crystals weighed 5.78 grams. A portion of the crystals was subjected to an analysis with the following result:

| | I. | II. | III. | Calculated for $C_{12}H_{22}O_{11}$. |
|---|---|---|---|---|
| C | 41.92 | 42.03 | 41.98 | 42.10 |
| H | 6.52 | 6.58 | 6.50 | 6.43 |
| O | | | | 51.47 |

Thus in composition the crystals correspond very closely with maltose. Crystallized maltose contains 1 molecule of $H_2O$, which, however, is completely driven off at 112–115°C. The crystals under examination were very soluble in water, sweet to the taste, and possessed the power of reducing alkaline copper solutions. A solution of the crystals was found to be dextro-rotary. The specific rotary power of the dried substance as determined by Wild's polaristrobometer in a 200 millimeter tube was +148.95° for sodium light. The specific rotary power of pure maltose as determined by O. Sullivan is +150°, by E. Schulze +149.5°.[1] The relative reducing power of the substance determined by means of Fehling's solution in the manner already described was found to be 67–68; the reducing power of pure maltose being 66; that is, 100 parts of maltose reduce as much copper oxide as 66 parts of dextrose.

The above results then show very conclusively that the crystalline product is maltose, thus confirming the previous results of Musculus and Mering,[2] and likewise of Dr. E. H. Bimmerman[3] and E. Kulz.[4]

A portion of the last alcohol-ether filtrate from the maltose precipitate left on evaporation a small residue, which was dextro-rotary and possessed of strong reducing power, presumably dextrose, though it was not subjected to a careful examination.[5] The three syrupy or gum-like precipitates obtained previous to the maltose precipitate by the addition of ether were all dextro-rotary and possessed of reducing power.

[1] See Sundwik on the specific rotary power of pure maltose. Zeitschrift für Physiolog. Chem. **5**, 427.

[2] Zeitschrift für Physiolog. Chem. **2**, 403.

[3] Pflüger's Archiv. **20**, 201. Also Report on Salivary Digestion in this Journal, **3**, 221.

[4] Pflüger's Archiv. **24**, 81.

[5] See Musculus and Mering.

# RESEARCHES ON THE COMPLEX INORGANIC ACIDS.[1]

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(Continued from Vol. 2, p. 294.)

## PHOSPHO-MOLYBDATES.

The application of molybdic oxide to the separation and estimation of phosphoric acid has given a special interest to the phospho-molybdates, and they have accordingly been studied more or less completely by several chemists. The most thorough investigations which we possess are those of Debray,[2] Rammelsberg,[3] and Finkener,[4] but particular salts have been examined by others, and these will be noticed under the appropriate special headings.

Phospho-molybdates appear to be formed whenever phosphoric acid or a soluble phosphate is brought into solution with a molybdate, the presence of a free acid not being essential. They are also formed when phosphates and molybdates are fused together, when molybdates insoluble in water are dissolved in phosphoric acid, when molybdic oxide is digested with an alkaline phosphate, and when insoluble phosphates and molybdates are treated together with a dilute acid. As a class, they are better defined and more easy to obtain pure than the phospho-tungstates, which in many respects they closely resemble. When phospho-molybdates of fixed alkaline bases are heated, they at first give off water of crystallization, and by careful heating may be obtained anhydrous. In some cases, however, molybdic oxide is volatilized even from salts containing fixed alkaline bases. I did not succeed in obtaining well-defined pyro-phospho-molybdates or pyro-phospho-tungstates, though of course the residues of the ignition of the acid salts may be regarded as such. When a phospho-molybdate is dissolved in ammonia-water and a current of sulphydric acid gas is passed into the hot solution, sulpho-molybdates are formed in large quantity. This reaction distinguishes the phospho-molybdates

[1] Proceedings Amer. Acad. of Arts and Sciences. Communicated by the Author.

[2] Bull. Soc. Chim. **2**, 404.

[3] Berichte deutsch. chem. Gesellschaft, **10**, 1776.

[4] Ibid. **11**, 1638.

from the phospho-tungstates, which are not decomposed under the same circumstances.

*Analytical Methods.*—The determination of the sum of the percentages of molybdic and phosphoric oxides was usually effected, as in the case of the phospho-tungstates, by precipitating the two oxides together by mercurous nitrate, with addition of mercuric oxide to neutralize the free nitric acid. It is best to precipitate from a boiling solution, and to boil for a short time after adding mercuric oxide. This last must always be in small excess. On account of the volatility of molybdic teroxide, it is not possible to determine directly the sum of the weights of the two oxides by simple ignition, but the difficulty may be readily overcome by the following process. The filter with the mercurous salts is to be cautiously heated in a platinum crucible properly inclined to the vertical axis of the flame until the filter is completely carbonized. On then regulating the heat and the supply of air, the carbon may be readily burned off, leaving a mass of mercurous salts mixed with more or less mercuric oxide, no weighable amount of molybdic teroxide being lost. An accurately weighed quantity of anhydrous normal sodic tungstate in fine powder is then to be added, and the contents of the crucible carefully mixed together with a stout platinum wire previously weighed with the crucible itself. The whole is to be heated at first by radiation from a small iron dish, and afterward directly, until a clear white fused mass is obtained. A second ignition and second weighing will determine whether every trace of mercury has been expelled. It is almost needless to remark that all these operations must be conducted under a flue with a good draught. This process gives excellent results, and is much less tedious than would perhaps be supposed.

After the estimation of the phosphoric oxide, the molybdic teroxide is best determined by difference from the sum of the weights of the two oxides found as above. No really good general method for the quantitative separation and estimation of molybdic oxide has yet been given, at least no one which is sufficiently accurate to serve as a check upon the method above described. The ammonium salts of this series are most simply analyzed by igniting them directly with sodic tungstate, when the loss of weight corresponds to the sum of the water and ammonia.

As in the case of the phospho-tungstates, the quantitative determination of the phosphoric oxide is a matter of considerable

difficulty. The method of separation by means of magnesia mixture has been carefully studied by Dr. Gooch, to whose paper I have already referred.[1] Dr. Gooch found it necessary to precipitate the ammonio-magnesic phosphate a second time, a single precipitation giving an error amounting sometimes to 6 or 7 per cent. of the phosphoric acid present. After re-solution and precipitation by ammonia, the mean error amounted to only 0.65 per cent., which makes an almost insensible correction when the quantity of phosphoric oxide is small. In a few instances I have applied this correction after a double precipitation, but I prefer to employ the following method, which gives an almost perfect separation from molybdic teroxide. The phosphoric oxide is first precipitated from a hot solution as ammonio-magnesic phosphate, the supernatant liquid after complete subsidence carefully decanted upon an asbestos filter, the precipitate washed with magnesia mixture and ammonia, then redissolved in the least possible quantity of hot dilute chlorhydric acid and reprecipitated with ammonia. After complete subsidence and decantation, the precipitate is boiled with successive portions of a solution of ammonic sulphide. A more or less dark orange-red solution of ammonic sulpho-molybdate is always obtained at first, but after two or three repetitions of the process the ammonic sulphide added remains colorless on heating. The ammonio-magnesian phosphate is then filtered upon the asbestos filter already employed. In place of this method I have sometimes employed the following modification, which gives, I think, equally good results. After the first precipitation the phosphate is to be redissolved, and the hot solution precipitated at once by ammonic sulphide in excess. The precipitated phosphate is then to be boiled two or three times with ammonic sulphide as above. Whatever inaccuracy is inherent in this method depends, in my judgment, upon the fact that, as Dr. Gooch has shown, the determination of phosphoric acid by means of magnesia is, under the most favorable circumstances, a less accurate process than has been supposed.

The determination of ammonia and the alkalies was effected by the methods already described in the case of the phospho-tungstates. Water must be estimated by ignition with sodic tungstate, as there is often volatilization of molybdic teroxide when a phosphomolybdate is ignited at a temperature sufficient to expel its water.

[1] Proceedings of American Academy, **15**, 53; and this Journal, **1**, 391.

The analyses require great care and no small amount of practice to insure good results. As in the case of the phospho-tungstates, the alkaline bases are best determined by difference.

*Twenty-four Atom Series.*—Phospho-molybdic acid. The acid of this series was first obtained by Debray, who prepared it by boiling ammonic phospho-molybdate with nitro-muriatic acid, and allowing the solution to evaporate spontaneously. I find that this is a good method of obtaining the acid, but the following details should be observed. The bright yellow ammonic phospho-molybdate should be first dried, and then heated with a large excess of strong aqua-regia in a casserole over an iron capsule to serve as a radiator. In this manner the decomposition proceeds very regularly and without succussions. When it becomes necessary to add fresh acid, the supernatant liquid should be allowed to settle completely and then be poured off carefully. Fresh acid may then be added, and the process, which is at best a slow one, continued. When the ammonium salt has disappeared, the liquid is to be evaporated until the excess of nitric and chlorhydric acids has been expelled. On standing, large bright yellow octahedral crystals are obtained from the very concentrated solution. These may be redissolved and recrystallized, but there is always some loss in the process of purification, because solution in water produces more or less decomposition of the acid with formation of a pale greenish white crystalline body. This substance passes very readily through a filter, and the solution of the acid must be allowed to settle completely before the clear supernatant liquid is brought upon the filter. Debray obtained three different hydrates of phospho-molybdic acid, to which he gave, respectively, the formulas

$$20MoO_3.P_2O_5.3H_2O+21aq,$$

$$20MoO_3.P_2O_5.3H_2O+48aq,$$

and

$$20MoO_3.P_2O_5.3H_2O+38aq.$$

Unfortunately, he has not given either the methods or the complete results of his analyses. In the first hydrate he found 13.30 per cent., in the second 23.40 per cent., and in the third 19.60 per cent. of water.

I obtained the acid only in transparent octahedral crystals which had a bright yellow color. Of these crystals, dried by pressure with woolen paper,

0.9945 gram lost by ignition with $WO_4Na_2$ 0.2362 gram=23.75 per cent. water.

1.4588 gram gave 0.0713 gram $P_2O_7Mg_2$=3.12 per cent. $P_2O_5$.

The analysis leads to the formula

$$24MoO_3.P_2O_5.3H_2O+59aq,$$

which requires:

| | | Calc'd. | Found. |
|---|---|---|---|
| $24MoO_3$ | 3456 | 73.31 | 73.13 |
| $P_2O_5$ | 142 | 3.01 | 3.12 |
| $62H_2O$ | 1116 | 23.68 | 23.75 |
| | 4714 | 100.00 | |

The phosphoric oxide was determined by double precipitation and treatment with ammonic sulphide. The molybdic oxide was estimated by difference. The crystallized acid effloresces so readily that the precise determination of the water is difficult. In a portion of the crystals which had effloresced in a very marked degree,—

0.9873 gram lost on ignition with $WO_4Na_2$ 0.1760 gram=17.82 per cent. water.

2.2472 grams gave 0.1163 gram $P_2O_7Mg_2$=3.31 per cent. $P_2O_5$.

The ratio of the molybdic to the phosphoric oxide is, in this analysis, also 24 : 1; and, if we compute the results of both analyses for an anhydrous compound of the two oxides, we find:

| | | Calc'd. | | |
|---|---|---|---|---|
| $24MoO_3$ | 3456 | 96.06 | 95.91 | 95 97 |
| $P_2O_5$ | 142 | 3.94 | 4.09 | 4.03 |
| | 3598 | 100.00 | 100.00 | 100.00 |

The analyses leave, I think, no reasonable doubt as to the ratio of the two oxides. Phospho-molybdic acid therefore corresponds in composition with phospho-tungstic acid, the ratio of the two oxides being 24 : 1, as given by Finkener,[1] and not 20 : 1, as stated by Debray. With respect, however, to the number of atoms of water in the crystallized octahedral hydrate, I may remark that, while the analysis agrees best with the formula given,

$$24MoO_3.P_2O_5.3H_2O+59aq,$$

[1] *Loc. cit.*

it is much more probable that the acid really contains an atom less of water, and that its formula, apart from the question of basicity, is

$$24MoO_3.P_2O_5.6H_2O+55aq,$$

like

$$24WO_3.P_2O_5.6H_2O+55aq,$$

already described. This formula requires 23.38 per cent. water, instead of 23.75 per cent., as found. Debray found 23.40 per cent. As already stated, the crystals analyzed were dried by pressure with woolen paper after draining off a syrupy mother liquor, and may therefore not have been perfectly free from extraneous water. Finally, the analyses of Finkener led also to the formula with 61 atoms of water, and I shall adopt this as the definite constitution of the octahedral hydrate. Finkener's work has not yet been published in detail; but, from the abstract which he has given, it clearly appears that we owe to him the establishment of the true constitution of the only phospho-molybdic acid yet obtained. As already mentioned, there are two other hydrates of phospho-tungstic acid having respectively the formulas

$$24WO_3.P_2O_5.6H_2O+47aq,$$

and

$$24WO_3.P_2O_5.6H_2O+34aq.$$

The two hydrates of phospho-molybdic acid described by Debray would correspond to the formulas

$$24MoO_3.P_2O_5.6H_2O+24aq,$$

and

$$24MoO_3.P_2O_5.6H_2O+43aq,$$

if we suppose them, as is most probable, to belong to the 24-atom series. The first formula requires 13.05 per cent., the second 19.66 per cent. water. Debray found 13.09 per cent. and 19.60 per cent. Finkener obtained still another hydrate, containing about 32 atoms of water, basic water included.

Phospho-molybdic acid dissolves very readily in water, forming a colorless liquid which has a strong acid reaction. As already stated, the solution is always accompanied by a slight decomposition, with formation of a very pale greenish white crystalline substance. A precisely similar decomposition is observed in the

solution of the corresponding phospho-tungstic acid. The crystals lose all their water when slightly ignited. According to Finkener, three atoms of water remain at 140°C. The solution readily expels carbonic dioxide from the alkaline carbonates. The question of the basicity of the acid will be discussed farther on.

24 : 3 *Ammonic Phospho-molybdate.*—The constitution of the beautiful yellow salt which is formed when an excess of a mineral acid is added to a solution containing molybdic and phosphoric oxides and a salt of ammonium, has long been in dispute. The analyses of Svanberg and Struve,[1] Nutzinger,[2] Sonnenschein,[3] Lipowitz,[4] and Seligsohn,[5] gave results which differed very sensibly from each other, according to the method of analysis employed. Debray gave the formula

$$20MoO_3.P_2O_5.3(NH_4)_2O+3aq,$$

but without the details of his analysis. More recently the subject has been examined with great care by Finkener,[6] who has arrived at the conclusion that, though the percentages of water and ammonia may vary within wide limits, the ratio of the molybdic and phosphoric oxides is always as 24 : 1.

With respect to the preparation and properties of the yellow ammonium salt, I have little to add to what has been done by these chemists. I repeatedly prepared the salt for analysis, usually by mixing solutions of ammonic molybdate—7 : 3 salt—and phosphate, adding nitric acid in excess to the solution, and boiling. When the mixed solution is boiled for a short time, the precipitation of the yellow salt is complete after standing until the liquid becomes cold. In the publication of this result, which is important in analysis, I have been anticipated by Atterberg;[7] but I propose in another paper to give the results of my work on the quantitative determination of phosphoric acid, and will then give ample details.

As regards the composition of the yellow phospho-molybdates of ammonium, my results do not agree with those of Finkener, as I think I have evidence that, as in the case of the phospho-tungstates, there are series of phospho-molybdates in which the ratio

[1] Journal für prakt. Chemie, **44**, 291.
[2] Pharmaceut. Vierteljahresschrift, **4**, 549.
[3] Journal für prakt. Chemie, **53**, 342.
[4] Poggendorff's Annalen, **109**, 135.
[5] Journal für prakt. Chemie, **67**, 470.
[6] *Loc. cit.*
[7] Berichte deutsch. chem. Gesellschaft, **14**, 1217.

of the molybdic to the phosphoric oxide is as 20 : 1, as 22 : 1, and as 24 : 1. In one preparation—

1.1492 gram lost on ignition with $WO_4Na_2$ 0.0827 gram $NH_3$ and $H_2O$=7.20 per cent.

0.5905 gram lost on ignition with $WO_4Na_2$ 0.0432 gram $NH_3$ and $H_2O$ = 7.31 per cent.

1.7158 gram gave 0.1027 gram $P_2O_7Mg_2$ = 3.83 per cent. $P_2O_5$.

0.9806 gram gave 0.0567 gram $P_2O_7Mg_2$ = 3.70 per cent. $P_2O_5$.

1.8903 gram gave 0.1321 gram $NH_4Cl$ = 3.20 per cent. $(NH_4)_2O$.

In these analyses the first determination of the phosphoric oxide was made by double precipitation only, without subsequent treatment with ammonic sulphide; but in the second, this reagent was employed in the manner above described. The ratio of $MoO_3$ to $P_2O_5$ is almost precisely 24 : 1, and the analyses correspond closely with the formula

$24MoO_3.P_2O_5.3(NH_4)_2O + 24MoO_3.P_2O_5.2(NH_4)_2O.H_2O + 16aq$,

which requires:

| | | Calc'd. | Mean. | | |
|---|---|---|---|---|---|
| $48MoO_3$ | 6912 | 89.05 | 89.00 | ... | ... |
| $2P_2O_5$ | 284 | 3.66 | 3.75 | 3.70 | 3.83 |
| $5(NH_4)_2O$ | 260 | 3.35 | 3.39 | 3.39 | |
| $17H_2O$ | 306 | 3.94 | 3.86 | 3.81 | 3.92 |
| | 7762 | 100.00 | 100.00 | | |

Acid salts of similar type occur frequently in the class of phosphomolybdates, as in that of phospho-tungstates.

24 : 1 *Croceo-cobalt Salt.*—The disposition of the cobaltamines to form highly crystalline compounds, together with their well-defined and various degrees of basicity, led me to study the relations of these bases to the phospho-molybdic acids. This had already been done to a certain extent with the 5 : 1 atom series by Jörgensen, whose results I shall cite in connection with that series. Neither roseo-cobalt nor luteo-cobalt forms well-defined salts with 24 : 1 phospho-molybdic acid. I had therefore recourse to croceo-cobalt,[1] the oxide of which may be written

$$Co_2(NH_3)_8(NO_2)_4O, \text{ or, briefly, } CcO.$$

The chloride of this series gives no precipitate with solutions of 7 : 3 ammonic molybdate, or of hydro-disodic phosphate; but in an

[1] Proceedings of American Academy, **10**, 1.

acid solution of these two salts a solution of the chloride throws down a beautiful bright yellow highly crystalline salt, which may be washed with cold water. The portion analyzed was dried on woollen paper only. Of this salt—

1.0728 gram gave 0.8133 gram $MoO_3+P_2O_5=75.81$ per cent.
1.4520 gram gave 0.4719 gram $P_2O_5=2.96$ per cent.

This corresponds to 72.85 per cent. $MoO_3$ by difference, and 24.19 per cent. of CcO and water by the loss. The analyses agree very closely with the formula

$$24MoO_3.P_2O_5.CcO.2H_2O+21aq,$$

which requires:

| | | Calc'd. | | |
|---|---|---|---|---|
| $24MoO_3$ | 3456 | 72.82 | | 72.86 |
| $P_2O_5$ | 142 | 2.99 | | 2.96 |
| CcO | 734 | 15.47 | 24.19 | 24.19 |
| $23H_2O$ | 414 | 8.72 | | |
| | 4746 | 100.00 | | |

Under the microscope this salt is seen to consist of fine yellow felted needles. It is very slightly soluble in cold water, but is soluble in a rather large quantity of boiling water, giving an orange yellow solution, with a strongly acid reaction. The solution gives with argentic nitrate a very insoluble sulphur-yellow flocky precipitate, which after a time becomes crystalline, and a pale yellow flocky precipitate with mercurous nitrate. No precipitate is formed with cupric sulphate or baric chloride. The salt could not be recrystallized; it is interesting as a particularly well-defined soluble acid salt of the 24 : 1 atom series.

24 : 2 *Acid Potassium Salt.*—This salt was prepared by boiling together solutions of potassic molybdate and phosphate, adding an excess of nitric acid, and boiling the whole for some time. As in the case of the ammonium salts, the precipitation is greatly facilitated by this process, taking place very slowly in the cold. The salt obtained was in very minute crystals, bright yellow, and but slightly soluble in cold water. Of this salt—

0.7772 gram lost on ignition 0.0128 gram = 1.64 per cent. water.
0.7962 " " 0.0130 " = 1.66 " "
1.1703 gram gave 1.0895 gram $MoO_3+P_2O_5=93.10$ per cent.
1.3263 gram gave 0.0779 gram $P_2O_7Mg_2=3.76$ per cent. $P_2O_5$.
1.3033 gram " 0.0778 gram " = 3.82 " "

The phosphoric oxide was twice precipitated as ammonio-magnesic phosphate. The analyses correspond with the formula

$$24MoO_3.P_2O_5.2K_2O.H_2O+3aq,$$

which requires:

| | | Calc'd. | | | | |
|---|---|---|---|---|---|---|
| $24MoO_3$ | 3456 | 89.55 | | 89.31 | | |
| $P_2O_5$ | 142 | 3.69 | 3.76 | | 3.82 | |
| $2K_2O$ | 189 | 4.90 | | 5.25 | | |
| $4H_2O$ | 72 | 1.86 | 1.66 | | 1.64 | |
| | 3859 | 100.00 | | | | |

*Twenty-two Atom Series.*—In the paper already referred to, Rammelsberg has described several salts in which he found the ratio of molybdic to phosphoric oxide as 22:1. Unfortunately, he has not given the method of analysis which he employed, and in a question of so much difficulty and delicacy it is, to say the least, extremely desirable to know what degree of precision may be expected in the analyses. As his results appear to be supported by my own, I shall adopt them, leaving to the further progress of analytical chemistry the final settlement of the few doubtful points.

22:3 *Ammonium Salt.*—Rammelsberg found for the neutral salt of this series the formula

$$22MoO_3.P_2O_5.3(NH_4)_2O+12aq,$$

which corresponds, except as regards the amount of water of crystallization, with a phospho-tungstate which I have already described—

$$22WO_3.P_2O_5.3(NH_4)_2O+21aq.$$

In one preparation of a yellow insoluble ammonium salt exactly resembling the corresponding salt of the 24-atom series—

1.6885 gram lost on ignition with $WO_4Na_2$ 0.0873 gram = 5.17 per cent. $NH_3$ and $H_2O$.

1.7764 gram gave 0.6200 gram $P_2O_7Mg_2$ = 4.17 per cent. $P_2O_5$.

1.9024 gram " 0.6029 gram " = 4.01 " "

1.2334 gram " 0.6262 gram $NH_4Cl$ = 4.23 " $(NH_4)_2O$.

The salt was dried for some time *in pleno* over sulphuric acid, and had evidently lost water of crystallization. If we deduct the

remaining water, 0.94 per cent., and calculate the analysis for an anhydrous salt, we have for the formula

$$22MoO_3.P_2O_5.3(NH_4)_2O;$$

| | | Calc'd. | |
|---|---|---|---|
| $22MoO_3$ | 3168 | 91.41 | 91.68 |
| $P_2O_5$ | 142 | 4.09 | 4.05 |
| $3(NH_4)_2O$ | 156 | 4.50 | 4.27 |
| | 3466 | 100.00 | |

In another preparation—

1.0324 gram lost on ignition with $WO_4Na_2$ 0.0922 gram = 8.93 per cent. $NH_3$ and $H_2O$.

2.0670 grams gave 0.1255 gram $P_2O_7Mg_2$ = 3.88 per cent. $P_2O_5$.

2.0352 grams " 0.1226 gram " = 3.84 " "

These analyses lead to the formula

$$22MoO_3.P_2O_5.3(NH_4)_2O+9aq,$$

which requires

| | | Calc'd. | | |
|---|---|---|---|---|
| $22MoO_3$ | 3168 | 87.32 | 87.21 | |
| $P_2O_5$ | 142 | 3.91 | 3.88 | 3.84 |
| $3(NH_4)_2O$ | 156 | 4.29 } 8.77 | 8.93 | |
| $9H_2O$ | 162 | 4.48 } | | |
| | 3628 | 100.00 | | |

If, from the analyses of the two salts above described, we calculate the composition of the combination of molybdic and phosphoric oxides supposed to be isolated, and compare this with the percentages calculated upon the two hypotheses of a ratio of 22 : 1 and a ratio of 24 : 1, we have—

| | | Calc'd. | I. | II. | Calc'd. | | |
|---|---|---|---|---|---|---|---|
| $22MoO_3$ | 3168 | 95.76 | 95.76 | 95.76 | 96.06 | 3456 | $24MoO_3$ |
| $P_2O_5$ | 142 | 4.24 | 4.24 | 4.24 | 3.94 | 142 | $P_2O_5$ |
| | 3310 | 100.00 | 100.00 | 100.00 | 100.00 | 3598 | |

In both cases the phosphoric acid was precipitated twice, but the ammonia-magnesian phosphate was not treated with ammonic

sulphide. According to the results of Dr. Gooch already cited, the probable error of this method does not exceed 1 per cent. in excess of the quantity of phosphoric oxide present. It appears, therefore, that the correction to be applied to the phosphoric oxide in the above analyses does not, at most, exceed 0.04 per cent. The mean of Dr. Gooch's analyses would require a deduction of 0.02 per cent. only. The yellow ammonium salt analyzed by Rammelsberg corresponds to the formula

$$22MoO_3.P_2O_5.3(NH_4)_2O+12aq,$$

which requires (Rammelsberg)—

| | | Calc'd. | |
|---|---|---|---|
| $22MoO_3$ | 3168 | 86.04 | 86.45 |
| $P_2O_5$ | 142 | 3.86 | 3.90 |
| $3(NH_4)_2O$ | 156 | 4.24 | 3.25 |
| $12H_2O$ | 216 | 5.86 | 5.77 |
| | 3682 | 100.00 | 99.37 |

Rammelsberg gives these figures as the means of several analyses which agree well with each other, but it must be admitted that a closer correspondence with the percentages required by the formulas would have been desirable. The comparison is not given in his paper. The air-dried salt loses all its water over sulphuric acid. The three atoms of basic water, if we assume their existence, must therefore be united by a very feeble affinity. Rammelsberg has also analyzed the corresponding potassic salt of the same series. I here give his results for the sake of comparison with the formula:

| | | Calc'd. | |
|---|---|---|---|
| $22MoO_3$ | 3168 | 83.17 | 84.43 |
| $P_2O_5$ | 142 | 3.73 | 3.78 |
| $3K_2O$ | 283 | 7.43 | 6.86 |
| $12H_2O$ | 216 | 5.67 | 5.55 |
| | 3809 | 100.00 | 100.62 |

This salt loses all its water between 120° and 140°. In judging the results of these analyses, as well as of those which I have given, it must be carefully borne in mind that the salts themselves cannot be recrystallized, and that consequently their absolute purity cannot

be guaranteed. Moreover, if—as I believe I have shown—there are very similar salts which represent three series in which the ratios of the molybdic and phosphoric oxides are respectively as 24 : 1, 22 : 1, and 20 : 1, we may, at least occasionally, have mixtures of the salts of three, or of any two series. The difficulty here is precisely that which occurs in the case of the phospho-tungstates.

44 : 2 *Acid Potassium Salt.*—This salt was prepared by boiling a mixture of potassic molybdate and phosphate with nitric acid in excess, when a beautiful yellow crystalline powder separated. This was washed with cold water and dried on woollen paper. Of this salt—

0.9850 gram lost on ignition 0.0521 gram = 5.28 per cent. water.
0.8983 gram gave 0.7943 gram $MoO_3+P_2O_5$ = 88.42 per cent.
2.0617 grams gave 0.1201 gram $P_2O_7Mg_2$ = 3.72 per cent.

These analyses lead to the formula

$$44MoO_3.2P_2O_5.5K_2O.H_2O+21aq,$$

or

$$22MoO_3.P_2O_5.3K_2O+22MoO_3.P_2O_5.2K_2O.H_2O+21aq,$$

which requires

| | | Calc'd. | |
|---|---|---|---|
| $44MoO_3$ | 6336 | 84.62 | 84.70 |
| $2P_2O_5$ | 284 | 3.79 | 3.72 |
| $5K_2O$ | 472 | 6.30 | 6.30 (diff.) |
| $22H_2O$ | 396 | 5.29 | 5.28 |
| | 7488 | 100.00 | |

The salt is therefore the acid salt corresponding to a neutral salt with the formula

$$22MoO_3.P_2O_5.3K_2O.$$

Rammelsberg's analyses agree better with the formula of the acid salt given above than with that of the neutral compound assumed by him.

*Twenty Atom Series.*—The only salt of this series which I have obtained is one of ammonium prepared like the salts already described, having like these a fine yellow color and a very fine grained crystalline structure, and, like them, but slightly soluble in water. Of this salt—

1.0936 gram lost on ignition with $WO_4Na_2$ 0.0729 gram = 6.66 per cent. $NH_3$ and $H_2O$.

1.8183 gram lost on ignition with $WO_4Na_2$ 0.1155 gram = 6.35 per cent. $NH_3$ and $H_2O$.

0.8862 gram gave 0.6153 gram $NH_4Cl$ = 4.12 per cent. $(NH_4)_2O$.

1.3213 gram gave 0.6224 gram $P_2O_7Mg_2$ = 4.19 per cent. $P_2O_5$.

1.5135 gram gave 0.6349 gram $P_2O_7Mg_2$ = 4.31 per cent. $P_2O_5$.

The salt was dried on a water bath, and afterward over sulphuric acid. The phosphoric oxide was precipitated twice, but not treated with ammonic sulphide. The analyses led to the formula

$$60MoO_3.3P_2O_5.8(NH_4)_2O.H_2O+11aq,$$

which requires—

| | | Calc'd. | | | | |
|---|---|---|---|---|---|---|
| $60MoO_3$ | 8640 | 89.09 | 93.48 | 89.21 | | 93.52 |
| $3P_2O_5$ | 426 | 4.39 | | 4.31 | 4.19 | |
| $8(NH_4)_2O$ | 416 | 4.29 | 6.52 | 4.12 | | 6.50 |
| $12H_2O$ | 216 | 2.23 | | 2.54 | | |
| | 9698 | 100.00 | | | | |

If we calculate the composition of the mixed oxides of molybdenum and phosphorus existing in this salt, we have—

| | | Calc'd. | |
|---|---|---|---|
| $20MoO_3$ | 2880 | 95.30 | 95.39 |
| $P_2O_5$ | 142 | 4.70 | 4.61 |
| | 3022 | 100.00 | 100.00 |

It will be seen that the ratio is here very nearly as 20 : 1. This may however be merely accidental, and farther researches are necessary to fully establish the existence of a 20-atom series.

According to Debray a solution of argentic nitrate gives with one of phospho-molybdic acid a precipitate which soon becomes crystalline, and which has the formula

$$20MoO_3.P_2O_5.7Ag_2O+24aq.$$

Such a salt would possess a twofold interest, first, as another evidence of the existence of a 20-atom series of phospho-molybdates, and, secondly, as showing that the acid of the series may unite with more than *six* atoms of base. On mixing the two solutions as above, I obtained a precipitate in small indistinct crystals of a greenish yellow color. These crystals were soluble in hot water,

but the solution was quickly decomposed with precipitation of a white powder. Under the microscope with a high power and transmitted light the salt appeared to consist of small tabular crystals mixed with a few long yellow prisms of very different habitus. Of this compound—

1.3604 gram lost by ignition with $WO_4Na_2$ 0.0692 gram water = 5.08 per cent.

2.1099 grams gave 0.8287 gram AgCl = 31.63 per cent. $Ag_2O$.

0.6733 gram gave 0.2619 gram AgCl = 31.44 per cent. $Ag_2O$.

2.1099 grams gave 0.0928 gram $P_2O_7Mg_2$ = 2.81 per cent. $P_2O_5$.

The phosphoric oxide was determined in the filtrate from the argentic chloride by double precipitation and treatment with ammonic sulphide. The ratio of the molybdic to the phosphoric oxide is as 21 : 1, but the formula which most nearly represents the analysis is

$$22MoO_3.P_2O_5.7Ag_2O+14aq,$$

which requires

| | | Calc'd. | | |
|---|---|---|---|---|
| $22MoO_3$ | 3168 | 61.08 | 60.57 | |
| $P_2O_5$ | 142 | 2.74 | 2.81 | |
| $7Ag_2O$ | 1624 | 31.32 | 31.44 | 31.63 |
| $14H_2O$ | 252 | 4.86 | 5.08 | |
| | 5186 | 100.00 | | |

The only conclusion which can fairly be drawn from the analysis is that there is at least one phospho-molybdate in which the number of atoms of base exceeds three. It is certain that the salt does not represent a perfectly definite and homogeneous compound, and it may possibly be a mixture of the 20-atom salt, $20MoO_3.P_2O_5.6Ag_2O$, and an acid molybdate of silver, $2MoO_3.Ag_2O$, nearly in atomic proportions. By dissolving the salt in nitric acid and evaporation, Debray obtained another salt in small brilliant yellow crystals. For this salt he proposes the formula

$$20MoO_3.P_2O_5.2Ag_2O+7aq,$$

but as usual he has given no analyses.

*Eighteen Atom Series.*—I have myself met with no salts belonging to this series, but according to Finkener[1] there are sodium salts corresponding to the general formula

$$18MoO_3.P_2O_5(3-x)Na_2O+(25+x)aq.$$

These salts are yellow and easily soluble.

[1] *Loc. cit.* p. 1639.

*Sixteen Atom Series.—16 : 3 Ammonium Salt.* In preparing the 5 : 3 atom ammonium salt a white crystalline precipitate was formed, insoluble in cold, but soluble with decomposition in much boiling water, and easily soluble in ammonia. In this salt dried over sulphuric acid,—

0.5100 gram lost by ignition with $WO_4Na_2$ 0.0722 gram = 14.16 per cent. $NH_3$ and $H_2O$.

1.1653 gram gave 0.1259 gram $NH_4Cl$ = 5.25 per cent. $(NH_4)_2O$.

0.8114 gram gave 0.0658 gram $P_2O_7Mg_2$ = 5.19 per cent. $P_2O_5$.

The analysis corresponds with the formula

$$16MoO_3.P_2O_5.3(NH_4)_2O+14aq,$$

which requires

| | | Calc'd. | Found. |
|---|---|---|---|
| $16MoO_3$ | 2304 | 80.73 | 80.65 |
| $P_2O_5$ | 142 | 4.97 | 5.19 |
| $3(NH_4)_2O$ | 156 | 5.46 | 5.25 |
| $14H_2O$ | 252 | 8.84 | 8.91 |
| | 2854 | 100.00 | |

*(To be continued.)*

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**Contributions from the Chemical Laboratory of Harvard College.**

## XIV.—PYROXANTHIN.[1]

By Henry B. Hill.

I have mentioned in an earlier paper[2] the yellow flocculent precipitate formed by the action of alkalies upon the crude furfurol, which upon examination proved to consist chiefly of pyroxanthin. This substance was discovered in 1835 by Dr. Scanlan,[3] of Dublin, in the residue from the preparation of methyl alcohol from crude wood spirit by means of lime. In 1836 it was further studied by Apjohn and Gregory,[4] who deduced from their analyses the for-

[1] Proceedings Amer. Academy of Arts and Sciences. Communicated by the Author.
[2] This Journal, **3**, 37.
[3] Phil. Mag. [3] **41**, 395.
[4] Royal Irish Acad. Proc. 1836, **33**. Ann. Chem. u. Pharm. **21**, 143.

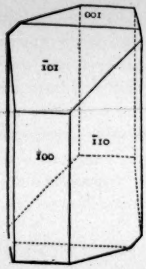
mula $C_{21}H_{18}O_4$, although they did not succeed in confirming this formula by the preparation and analysis of any of its derivatives. This formula was subsequently changed to $C_{10}H_8O_2$ by Gmelin,[1] although this change was apparently not based upon any further experimental work. Although I have not as yet had any very considerable quantity of material at my command, I have studied some of its reactions, and prepared two well-marked bromine derivatives whose percentage composition necessitates the adoption of the formula $C_{15}H_{12}O_3$.

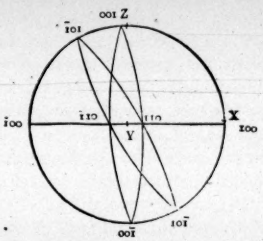
In the method I have described for the purification of the crude furfurol, after that portion which is volatile with steam has been distilled off, there remains a red viscous oil in the retort, which, on cooling, partially solidifies. If this semi-solid mass is then treated with small quantities of cold alcohol, the red oil, which results, in part at least, from the action of the sodic hydrate upon the furfurol, dissolves, while the greater part of the pyroxanthin is left behind in minute crystals. Occasionally, this viscous residue crystallizes only after the addition of the alcohol and vigorous stirring. The pyroxanthin seems to be more neatly separated, if the furfurol is slightly acidified with acetic acid after separating the alkaline solution before distilling with steam. After the crystals have been well washed with cold alcohol, they are recrystallized from boiling alcohol until the substance has a bright, clear, orange-yellow color. Boiling the alcoholic solution with bone-black facilitates the removal of the red impurities.

Pyroxanthin is completely insoluble in water, and very sparingly soluble in ether or carbonic disulphide; in hot alcohol, benzol, or glacial acetic acid it dissolves abundantly, and crystallizes in well-developed forms on cooling. From alcohol it crystallizes in small, brilliant, orange-yellow needles with a blue reflex; from benzol in tolerably large reddish-yellow monoclinic prisms; and from glacial acetic acids in flat radiated needles, which are formed by the development of the prism in the direction of the orthodiagonal. The crystallographic examination which I made of the substance gave the following results:

[1] Gmelin's Handbuch, 7, 157.

CRYSTALLINE FORM OF PYROXANTHIN.




*Monoclinic System.*

Forms observed $\{001\}$ $\{\bar{1}01\}$ $\{10\bar{1}\}$ $\{110\}$.

$a : b : c = 2.748 : 1 : 1.413$ $ac = 87° 56'$

*Angles between Normals.*

| | Found. | Calculated. |
|---|---|---|
| 110 : $\bar{1}$10 | 40° 1′ | Fundamental angles. |
| $\bar{1}$01 : 001 | 26° 46′ | Fundamental angles. |
| $\bar{1}$01 : $\bar{1}$00 | 61° 10′ | Fundamental angles. |
| 110 : 00 | 69° 54′ | 69° 59′ |
| $\bar{1}$10 : $\bar{1}$01 | 80° 25′ | 80° 30′ |

For analysis the substance was crystallized from alcohol and dried at 100°.

I. 0.2673 gram substance gave 0.7341 gram $CO_2$ and 0.1279 gram $H_2O$.

II. 0.2432 gram substance gave 0.6690 gram $CO_2$ and 0.1841 gram $H_2O$.

| | Calculated for $C_{13}H_{12}O_3$. | Found. I. | Found. II. | Apjohn and Gregory. |
|---|---|---|---|---|
| C | 75.00 | 74.91 | 75.01 | 74.27 |
| H | 5.00 | 5.31 | 5.25 | 5.61 |

Since the substance was very refractory and needed a high temperature in a stream of oxygen for complete combustion, my results

show a sufficiently close agreement with those of Apjohn and Gregory.

This substance melts at 162° and volatilizes with partial decomposition at a higher temperature, although it may be sublimed without difficulty by careful heating in a current of air. In concentrated sulphuric acid it dissolves with an intense purple, and in hydrochloric or hydrobromic acid with a crimson color. From these solutions water precipitates the substance apparently unchanged. In alkaline solutions it is completely insoluble, and by melting caustic potash it is merely carbonized. Bromine attacks it vigorously, and, under certain conditions, forms well-crystallized products.

*Dibrompyroxanthintetrabromide*, $C_5H_{10}Br_2O_2Br_4$. When pyroxanthin is suspended in ten times its weight of carbonic disulphide, and three and a half parts of bromide diluted with an equal weight of carbonic disulphide are added, the pyroxanthin instantly dissolves and forms a clear deep-red solution. After standing for a short time, clouds of hydrobromic acid are given off, and soon after the separation of a beautifully crystalline substance begins. After twenty-four hours the carbonic disulphide is poured off, and the crystals which have separated are thoroughly washed with ether. For analysis I recrystallized the substance from boiling chloroform and dried it *in vacuo*.

I. 0.5598 gram substance gave 0.5136 gram $CO_2$ and 0.0842 gram $H_2O$.

II. 0.6814 gram substance gave 0.5758 gram $CO_2$ and 0.0845 gram $H_2O$.

III. 0.3094 gram substance gave 0.4884 gram AgBr.[1]

IV. 0.3128 gram substance gave 0.4936 gram AgBr.

| | Calculated for $C_{10}H_{10}Br_6O_2$. | Found. | | | |
|---|---|---|---|---|---|
| | | I. | II. | III. | IV. |
| C | 25.07 | 25.02 | 24.87 | | |
| H | 1.39 | 1.67 | 1.49 | | |
| Br | 66.85 | | | 67.16 | 67.13 |

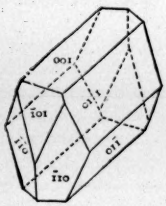
These percentages agree closely with those required by the formula $C_{15}H_{10}Br_6O_2$, and the behavior of the substance is such that it must be considered dibrompyroxanthintetrabromide. It crystallizes in small, brilliant, colorless prisms which belong to the triclinic system. On heating, it is decomposed below 100° with carbonization and the evolution of hydrobromic acid. It is very sparingly

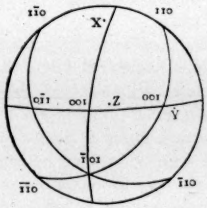
[1] See note, 3, 42.

soluble in ether or carbonic disulphide; in boiling benzol or chloroform it dissolves quite freely, and the greater part again separates on cooling. In cold alcohol or glacial acetic acid, it is sparingly soluble; but, on warming, it dissolves with decomposition and then forms a yellow solution. In the cold, it is unaltered by concentrated sulphuric acid; on heating, it is carbonized.

A crystallographic study of the substance gave the following results:

CRYSTALLINE FORM OF DIBROMPYROXANTHINTETRABROMIDE.




*Triclinic System.*

Forms observed, {001} {011} {01$\bar{1}$} {110} {$\bar{1}$10} {$\bar{1}$01}.

$a : b : c = 0.733 : 1 : 2.370.$

$bc = 74° 43'$; $ac = 83° 40'$; $ab = 96° 46'$.

*Angles between Normals.*

| | Found. | Calculated. | |
|---|---|---|---|
| $0\bar{1}1 : \bar{1}\bar{1}0$ . . . . | 47° 15′ | | Fundamental angles. |
| $0\bar{1}1 : \bar{1}01$ | 69° 50′ | | |
| $0\bar{1}1 : 011$ | 135° 27′ | | |
| $\bar{1}\bar{1}0 : \bar{1}01$ | 34° 18′ | | |
| $\bar{1}\bar{1}0 : \bar{1}10$ | 76° 57′ | | |
| $\bar{1}01 : \bar{1}10$ | 48° 49′ | 48° 58′ | |
| $\bar{1}10 : 01\bar{1}$ | 61° 14′ | 61° 12′ | |
| $\bar{1}10 : 011$ | 58° 6′ | 57° 41′ | |
| $001 : \bar{1}\bar{1}0$ | 73° 59′ | 74° 18′ | |
| $001 : \bar{1}10$ | 93° 8′ | 93° 41′ | |
| $001 : 0\bar{1}1$ | 54° 6′ | 53° 49′ | |
| $001 : 011$ | 81° 21′ | 81° 33′ | |
| $001 : 101$ | 63° 37′ | 63° 57′ | |

Bromine when moderately diluted with carbonic disulphide has no further action upon this substance. It is attacked, however, when exposed to the vapors of bromine, and deliquesces rapidly, forming a dark-red syrup, which over lime *in vacuo* gradually solidifies. From this product I have as yet been unable to isolate any substance with characters sufficiently well marked to encourage further study.

*Dibrompyroxanthin*, $C_{15}H_{10}Br_2O_3$. The subtraction of bromine, on the other hand, gave a beautifully crystalline product with sharply marked characteristics. This substance I first made by the action of phenol. If the dibrompyroxanthintetrabromide is gently warmed with a little phenol, to which sufficient water has been added to keep it liquid, it dissolves, forming a highly colored solution, which is red by transmitted and green by reflected light. If alcohol is then added, it causes the separation of an abundance of fine, felted brilliant-yellow needles, which may be recrystallized from alcohol. This same substance may also be made by boiling the tetrabromide with absolute alcohol, and adding zinc dust or finely powdered metallic antimony. The latter method is perhaps most advantageous, since little or no product is obtained if the phenol solution is too strongly heated, or if the zinc dust contains a large percentage of oxide. For analysis, the substance was dried at 100° after several recrystallizations from alcohol. The material used in analyses I. and II. was made with phenol, while that used in analysis III. was made with antimony.

I. 0.3816 gram substance gave 0.6333 gram $CO_2$ and 0.0918 gram $H_2O$.

II. 0.3137 gram substance gave 0.2978 gram AgBr.

III. 0.2577 gram substance gave 0.2419 gram AgBr.

| Calculated for $C_{15}H_{10}Br_2O_3$. | | Found. | | |
|---|---|---|---|---|
| | | I. | II. | III. |
| C | 45.22 | 45.25 | | |
| H | 2.51 | 2.67 | | |
| Br | 40.20 | | 40.40 | 39.94 |

The analyses showed that the substance was dibrompyroxanthin, and that it was formed from the bromine derivative already described by the subtraction of bromine.

In hot alcohol it dissolves readily, although in cold it is sparingly soluble. It is quite soluble in ether or carbonic disulphide, and very readily in benzol, chloroform, or glacial acetic acid.

From a solution in warm chloroform, it crystallizes in large, compact, twinned forms of the monoclinic system, which are dichroic. In concentrated sulphuric acid, it dissolves with an intense, pure blue color. This blue solution, on dilution with water, throws down a yellow precipitate, which is apparently the unchanged substance. If quickly heated upon platinum foil, it melts to a perfectly clear yellow liquid; but it is impossible to determine its melting point, since it decomposes and carbonizes when its temperature is more gradually raised. A solution in carbonic disulphide, when mixed with bromine, gradually deposits well-formed crystals of the tetrabromide. This simple substitution product I have not succeeded in making directly from pyroxanthin. In every case where a smaller quantity of bromine was employed, the addition product was still formed, and a part of the pyroxanthin remained unaltered.

I have also studied the action of aqueous bromine, but have not been successful in obtaining any definite products. If pyroxanthin is suspended in water, and bromine gradually added, or the vapors of bromine carried in by a current air, a white amorphous substance is slowly formed, which is almost insoluble in water, but extremely soluble in other ordinary solvents. By evaporation of such solutions, the substance again separates in an amorphous condition. In alkalies it dissolves, forming a deep-brown solution, from which nothing can be precipitated by the addition of acids.

Since there appeared to be little hope of effecting its purification by ordinary methods, I proceeded to analyze carefully prepared material. I found, however, that the substance turned brown on standing over sulphuric acid, and the analysis of two different preparations showed conclusively that no constant results could be obtained in this way.

I. 0.3726 gram substance gave 0.3142 gram $CO_2$ and 0.0594 gram $H_2O$.

II. 0.2016 gram of the same preparation gave 0.2773 gram AgBr.

III. 0.5255 gram substance gave 0.4142 gram $CO_2$ and 0.0734 gram $H_2O$.

IV. 0.3853 gram of the same preparation gave 0.5731 gram AgBr.

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| C | 23.00 | | 21.50 | |
| H | 1.77 | | 1.55 | |
| Br | | 58.53 | | 63.30 |

These results showed merely that oxidation had taken place together with the substitution of hydrogen by bromine.

On boiling with bromine-water, total decomposition seemed to ensue, and no definite products could be isolated except oxalic acid and a small quantity of a volatile oil which had the odor of bromoform, and gave the characteristic odor of phenyl isocyanide when heated with anilin and alcoholic potash.

Although I have already carried on the investigation of pyroxanthin in several other directions, I have not as yet been able to study the reactions involved as much in detail as I could wish, and I must therefore reserve for a subsequent paper all description of these experiments.

Concerning the origin and mode of formation of the pyroxanthin, I can at present add nothing. Its high melting point, and its general behavior when compared with the properties of the oil from which it is made, lead directly to the conclusion that it results either from polymerization or condensation. Its formula, $C_{15}H_{12}O_3$, naturally suggests a trimolecular polymeric form; the composition of its bromine derivatives, on the other hand, favors rather the view that its molecule is the product of condensation.

Schweizer,[1] in 1848, prepared from pyroligneous acid an oil to which he gave the name pyroxanthogen, as the substance from which the pyroxanthin was formed. He attempted no explanation of the mode of formation, and made no analysis of his product. Although his description is not very precise, it is sufficient to show that it was a mixture tolerably complex in its nature.

All my own attempts to isolate from the crude furfurol the substance essential to the formation of the pyroxanthin have been unsuccessful. Its separation from the furfurol is a matter of some difficulty, not only on account of the small quantities present, but also since it appears to be closely allied to furfurol. In its boiling point or in its behavior towards reagents, I have as yet found no differences sufficiently well marked to form the basis for a method of separation.

For the present, at least, a more careful study of the pyroxanthin itself would seem to be the most speedy way to discover the mode of its formation.

[1] Jour. pract. Chem. **44**, 129.

Laboratory Notes from the University of Cincinnati.

## XXIII.—THE SPEED OF SAPONIFICATION OF ETHYL ACETATE.[1]

By R. B. Warder.

The term saponification, in its general sense, implies the separation of the alcoholic and the acid radical of a compound ether. For example, acetic ether may be decomposed by various means as follows:

1. $C_2H_5.O.C_2H_3O+HOH=C_2H_5OH+HOC_2H_3O.$
2. $C_2H_5.O.C_2H_3O+Na_2CO_3+H_2O$
$=C_2H_5OH+NaOC_2H_3O+HNaCO_3.$
3. $C_2H_5.O.C_2H_3O+HNaCO_3=C_2H_5OH+NaOC_2H_3O+CO_2.$
4. $C_2H_5.O.C_2H_3O+NaOH=C_2H_5OH+NaOC_2H_3O.$

The first of these reactions has already received some attention, directly and indirectly, in connection with experimental and theoretical researches on the speed and limits of etherification.[2] The study of the second reaction would doubtless be complicated by the third; and by the thermal relations of $CO_2$ to the solvent employed. The sesquicarbonate may give rise to still another simultaneous reaction. The saponification by sodic hydrate, although too rapid for the most convenient and accurate study, appears to represent a single metathetical operation; and the fourth reaction was accordingly selected for this part of the present research.

### I.—Method of Experiment.

Dilute aqueous solutions of ethyl acetate and sodic hydrate, of known strength and volume, were quickly mixed together. At the end of a suitable interval, the alkali still remaining was quickly neutralized with excess of standard oxalic acid. The volume of acid required shows at once the amount of alkali present when the

[1] Some of the results contained in this paper have also appeared in Ber. **14**, 1361, and in this Journal, **3**, 203 and 294.

[2] See Berthelot and St. Gilles, Ann. chim. phys. [3] **65**, 385; **66**, 5; **68**, 225. Berthelot, Ann. chim. phys. [3] **66**, 110; [5] **14**, 437; **15**, 220. J. H. van't Hoff, Ber. **10**, 669. Menschutkin, Ann. Chem. **195**, 334; **197**, 193.

action was interrupted; whence the quantities of alkali and ether that have neutralized each other are found by difference. In making several determinations with the same mixture (as in Series I. and II., below), successive portions were drawn off to be neutralized at convenient intervals.

The absorption of carbon dioxide, by diminishing the intensity of the reaction, proved to be a source of error requiring special precautions. The soda solution was kept in a large bottle provided with soda-lime ventilator, and a syphon, through which it was drawn into the outlet of an ordinary burette. The latter was protected in the same manner, so that the alkali was completely shielded from the atmosphere, until it was measured from the burette into the experimental flask, to be mixed with the ether. This flask was likewise provided with soda-lime ventilator, and with a discharge pipe, through which successive portions were measured out with the pipette, without the admission of non-purified air.

It was not practicable to use a perfectly caustic soda solution, as usually prepared for alkalimetry with excess of calcic hydrate, because the still undetermined rate of saponification by lime would have complicated the problem. I therefore selected a nearly pure sample of soda, and made frequent determinations of its causticity. The distilled water used in dilution also contained traces of carbon dioxide, the effect of which was eliminated from the final results. Preliminary experiments showed that the direct action of water and small quantities of sodic carbonate, at ordinary temperatures, may be neglected in determinations of the far more rapid action of sodic hydrate. The titrations were made with phenol phthalein as indicator, by a method (similar to that of Lux[1]) which was expressly investigated[2] to meet the requirements of this research. If $A_1$ is the quantity of acid required to discharge the red color in the cold, and $A_2$ is the additional amount needed to effect permanent decolorization when boiled, $A_1 - A_2$ represents the caustic alkali present.

## II.—Formulae for the Interpretation of Results.

A fundamental dynamical theorem of the "action of mass" was stated by Berthelot[3] in 1862, with regard to the formation of ethers,

[1] Zeitsch. anal. Chem. **19**, 457. [2] This Journal, **3**, 55, 232. [3] Ann. chim. phys. [3] **66**, 112

as follows: "The quantity of ether formed at each instant is proportional to the product of the active masses present." Various experimenters have shown that the same law applies to several other reactions that take place in a homogeneous fluid, and the mathematical consequences have already been pretty fully developed.[1] A brief resumé is here given, so far as the formulae are required for the purposes of the present paper.

The fundamental theorem for the action of mass is expressed in the equation

$$\frac{-du}{dt} = auv \qquad (I)$$

where $u$ and $v$ are the masses of the two active bodies present at at any moment, the differential coefficient $\frac{-du}{dt}$ is the speed of the action by which $u$ is diminished, and $a$ is some constant which depends upon the intensity of the chemical affinities, the temperature, and other conditions. To apply this formula, it will be convenient to use those units of mass and volume which are generally employed in volumetric analysis; that is, with 1 cc. as a unit of volume, let the chemical equivalent of each substance expressed in milligrams be the unit of mass for that particular substance; thus, the unit of NaOH is 40 mg., that of $Na_2CO_3$ is 53 mg., etc. If the symbols $u$ and $v$ represent the quantities present in the unit of volume, they express the concentration of the solution with respect to the two bodies, where unity denotes a normal solution, 0.1 denotes a decinormal solution, and so on.

Let $u_0$, $v_0$ = the concentration at the beginning of any interval, and $u_t$, $v_t$ = the concentration at the end of the same; then, since equivalent amounts of the two active bodies are simultaneously rendered inactive by simple metathesis, $v_t - u_t = b$, which is a constant, independent of the interval $t$.

Hence, $$\frac{-du}{dt} = au(u+b); \frac{-du}{u(u+b)} = adt. \qquad (II)$$

When the two substances are present in equivalent amounts, $b = 0$, and

$$\frac{-du}{u^2} = adt. \qquad (2)^2$$

[1] Berthelot, *loc. cit.* J. H. van't Hoff, *loc. cit.* Hood, Phil. Mag. [5] **6**, 371; **8**, 121. Guldberg and Waage, J. pr. Chem. [2] **19**, 69, etc. Muir, Phil. Mag. [5] **8**, 181.

[2] The more general equations are distinguished in this paper by Roman numerals; those which apply only under the restriction that $b = 0$, by Arabic numerals.

By integrating equation II.,

$$l_e\left(\frac{u_t+b}{u_t}\right)=abt+l_e\left(\frac{u_0+b}{u_0}\right) \qquad \text{(III)}$$

$$\therefore\ a=\frac{l_e\left(\frac{u_t+b}{u_t}\cdot\frac{u_0}{u_0+b}\right)}{bt}=\frac{\log.\left(\frac{u_t+b}{u_t}\cdot\frac{u_0}{u_0+b}\right)}{0.4343bt} \qquad \text{(IV)}$$

where $l_e$ represents the Naperian logarithm and log. represents the common logarithm.

Likewise from eq. (2) we find

$$u_t=\frac{u_0}{au_0\,t+1} \qquad (3)$$

$$\therefore\ a=\frac{u_0-u_t}{u_0u_t\,t} \qquad (4)$$

It may sometimes be desirable to eliminate the effect of any irregularity during the process of mixing the two substances; for this purpose eq. (4) may take the form

$$a=\frac{u_0'-u_t}{u_0u_t\,t'} \qquad (5)$$

where $u_0'$ = the value of $u$ as determined by the first titration of a series, and the interval, $t'$, is counted from this titration.

When $b$ is very small in comparison with $u_0$ and $u$, the formula

$$a=\frac{u_0-u_t}{u_0u_t\,t}\cdot\frac{u_0+u_t}{u_0+u_t+2b} \qquad \text{(V)}$$

gives a close approximation to the correct value.

It may be observed that the curve representing the relation between $u$ and $t$ may vary from an equilateral hyperbola (when $b=0$) to a logarithmic curve (when $b=\infty$); and eq. (V) nearly expresses the former, if $b$ is very small.

Equation (IV), (4), (5) or (V) (according to the conditions of the experiment) affords a valuable criterion in researches on the speed of chemical action. Where the initial conditions are known, each determination of $u$, at the end of a measured interval, $t$, is sufficient to deduce a value for $a$, which may be called the "coefficient of speed"; and if the reaction is one of simple metathesis, and not affected by any disturbing change of conditions, the theorem requires that a series of observations shall give nearly

agreeing values for $a$. A disturbing cause,[1] on the other hand, may often be detected by a series of determinations in which the values deduced for $a$ are found to increase or decrease with some regularity.

It is evident that the rate of chemical action in dilute aqueous solution will depend in part upon the rate of diffusion by which the active bodies are continually being brought into contact. Schuhmeister[2] has shown that when the concentration of the haloid salts of potassium is reduced from 0.3 per cent. to 0.1 per cent. the diffusion constant is diminished by nearly 11 per cent. It is probable, therefore, that a more complete investigation of the theory of the action of mass in very dilute solution will require a modification of the above equations, by substituting for $a$ in eq. (I) some function of $u$ and $v$.

## III.—Application of the Theorem and Formulae to Saponification by Sodic Hydrate.

The ethyl acetate used had neutral reaction, but was not constant in its boiling point. Titrated by Wanklyn's[3] method, it neutralized 93.63 per cent., 93.42 per cent. and 94.41 per cent. of the theoretical quantity of alkali. As a mean result, 93.82 per cent. of acetate was found to be present; hence a normal solution would require 93.80 grams to the litre. The impurity had a low boiling point, and seemed to consist chiefly of ethyl oxide. Qualitative tests for water and free alcohol gave negative results. A $\frac{1}{2}$ normal solution was readily prepared by weighing out the required amount of the ether in a $\frac{1}{2}$ litre flask, and filling up to the mark with water; but after a short time bubbles of gas or vapor were seen to separate upon the sides of the burette, perhaps consisting of ethyl oxide, and requiring some watchfulness in measuring.

The acid used was $\frac{1}{2}$ normal, carefully standardized with pure sodic carbonate.

The soda solution was approximately $\frac{1}{2}$ normal.

For 18.85 cc. alkali, $A_1 = 19.22$, $A_2 = 0.17$, $A_1 - A_2 = 19.05$ cc.

" 23.60 " $A_1 = 24.07$, $A_2 = 0.19$, $A_1 - A_2 = 23.88$ cc.

From these determinations (which were made on different days) the caustic alkali is found to be $\frac{1.010}{8}$ normal and $\frac{1.012}{8}$ normal; the mean factor is $\frac{1.011}{8}$. The amount of caustic soda was very

[1] Harcourt and Esson discuss a remarkable case, in which the manganous sulphate formed by the action of $K_2Mn_2O_8$ and $H_2SO_4$ upon $C_2H_2O_4$ *accelerates* that action.—Chem. Soc. J. **20**, 460.

[2] Wien. Acad. Ber. April 1879, and Beibl. zu Ann. Phys. **3**, 682.

[3] Chem. Soc. J. [2] **5**, 170.

slightly diminished by the short exposure to air in the process of measuring, and by traces of $CO_2$ in the distilled water added; hence the value of $A_2$ was also determined after saponification. In the very dilute solutions to be titrated, this was rendered the more difficult from the presence of sodic acetate, which is decomposed on long boiling, and gradually acquires alkaline reaction towards phenol phthalein. The correction for the carbonate is so small, however, that this error will not invalidate the general result obtained in the following series:

*Series I.* Temperature was 20.5° to 20.6°. A mixture was prepared, consisting of

501 cc. water,
99 " $\frac{1.01}{8}$ normal NaOH, and
25 " $\frac{1}{2}$ " $C_2H_5.O.C_2H_3O$;

making 625 " in all; which was thus a $\frac{1}{50}$ normal solution of alkali and ether; that is, $u_0 = v_0 = 0.02$. 100 cc. were drawn out for each titration. A mean value of 0.35 cc. was assumed for $A_2$, in each determination of causticity. The observed values of $A_1 - A_2$ are compared below with those calculated from the mean value deduced for $a$. The time is expressed in minutes.

| Time. | $A_1 - A_2$ Observed. | $A_1 - A_2$ Calculated. | Errors. | $a = \frac{u_0 - u_t}{u_0 u_t t}$ |
|---|---|---|---|---|
| 5 | 10.24 cc. | 10.36 | — 0.12 | 5.625 |
| 15 | 6.13 | 6.07 | + .06 | 5.37 |
| 25 | 4.32 | 4.29 | .03 | 5.405 |
| 35 | 3.41 | 3.32 | .09 | 5.27 |
| 55 | 2.31 | 2.29 | .02 | 5.385 |
| 120 | 1.10 | 1.13 | — .03 | 5.645 |

Mean value of $a = 5.45$

*Series II.* Temperature was 21.0° to 21.3°. The same quantities were taken as in Series I. $A_2 = 0.35$.

| Time. | $A_1 - A_2$ Observed. | $A_1 - A_2$ Calculated. | Errors. | $a = \frac{u_0 - u^t}{u_0 u_t t}$ |
|---|---|---|---|---|
| 5 | 10.15 cc. | 10.26 | — 0.11 | 5.765 |
| 15 | 6.06 | 5.97 | + .09 | 5.465 |
| 25 | 4.23 | 4.21 | .02 | 5.57 |
| 35 | 3.29 | 3.25 | .04 | 5.52 |
| 45 | 2.61 | 2.65 | — .04 | 5.70 |

Mean value of $a = 5.60$

The calculated and observed values for $A_1$—$A_2$ show a pretty fair agreement with the fundamental theorem, and indicate that the process is nearly free rom secondary reactions or other disturbing causes.

If the initial period of action is eliminated by formula (5), the mean results found above are reduced to $a = 5.35$ at 20.5° to 20.6° and $a = 5.50$ at 21.0° to 21.3°; hence the values obtained by making a single titration under the conditions of these series are probably liable to be a little too high. The significance of the values found for $a$ will be readily deduced from eq. I. by making $u$ and $v$ each equal to unity. The "coefficient of speed" then appears as *the number of milligram-equivalents per cc. which* (according to the accepted theory of the action of mass) *would react upon each other in one minute, in a solution kept at normal strength.*

It must be stated, however, that in several series of experiments the calculated value of $a$ was found to diminish steadily instead of being constant, even with the precautions described above; so that further examination may possibly indicate how the fundamental theorem and resulting formulae must be modified, in order to include any necessary correction for variation in the diffusion constant, etc., as already suggested. Circumstances prevented a more thorough investigation, at this time, of some possible causes of variation in the experimental results; and the fundamental theorem is accepted with regard to the reaction studied, as representing a sufficiently close approximation to the truth. Even if the values deduced for $a$ should not have the exact value defined above, they will yet serve for the comparison drawn in the next section.

## IV.—Influence of Temperature.

To study the relation between the coefficient of speed and the temperature, I prepared two liters of $\frac{1}{32}$ normal ether solution. For each determination I drew out 100 cc., cooled or warmed it as might be desired, added about 25 cc. of $\frac{1.01}{8}$ normal HNaO, corked tightly, and maintained a nearly constant temperature until the moment arrived for adding the standard oxalic acid. The period of action was made to vary from twenty minutes at low temperatures to four minutes at the highest temperature, in order to secure favorable conditions for accurate measurement, the action being generally arrested when about half the ether had been saponi-

fied. Since 100 cc. of $\frac{1}{32}$ normal ether solution was increased to a volume of 125 cc., the mixture was $\frac{1}{40}$ normal with regard to the ether, or $u_0 = 0.025$. The alkali was added from a full burette, about 10 seconds being required for the desired amount to flow out. Ten minutes were generally allowed before taking the final reading of the burette, that the surface of the somewhat viscous solution might become stationary. The initial quantity of NaOH was carefully estimated from the volume taken in each case, its original strength, and the traces neutralized by $CO_2$, on flowing into the solution of ether. The values of $u_0$ and $v_0$ in no case differed more than two to three per cent., and usually the difference was much less. In the determinations of causticity, a mean value of 0.5 cc. was assumed for $A_2$ throughout this series. The numerical results obtained, as calculated by eq. (V), are given in the following table, as the "observed" values of $a$. The mean temperatures are given under $t$; variations of some tenths of a degree could not be avoided with the appliances used. The "calculated" values of $a$ are obtained by means of various empirical formulae, as explained below.

SERIES III.

| | $a$ | $a$ calculated. | | |
|---|---|---|---|---|
| $t$. | Observed. | A. | B. | C. |
| 3.6°C | 1.418 | 1.351 | 1.585 | 1.543 |
| 5.5 | 1.680 | 1.645 | 1.695 | 1.684 |
| 6.0 | 1.782 | 1.728 | 1.735 | 1.731 |
| 6.6 | 1.730 | 1.826 | 1.788 | 1.793 |
| 7.2 | 1.920 | 1.928 | 1.848 | 1.861 |
| 11.0 | 2.563 | 2.623 | 2.373 | 2.428 |
| 12.4 | 2.788 | 2.906 | 2.630 | 2.707 |
| 12.7 | 2.875 | 2.969 | 2.690 | 2.768 |
| 19.3 | 4.568 | 4.567 | 4.403 | 4.490 |
| 20.0 | 4.732 | 4.771 | 4.630 | 4.716 |
| 20.4 | 4.779 | 4.882 | 4.763 | 4.848 |
| 20.9 | 4.989 | 5.031 | 4.934 | 5.018 |
| 23.6 | 6.010 | 5.903 | 5.933 | 6.003 |
| 27.0 | 7.243 | 7.186 | 7.371 | 7.414 |
| 28.4 | 8.034 | 7.786 | 8.022 | 8.049 |
| 30.4 | 8.876 | 8.740 | 9.013 | 9.014 |
| 32.9 | 9.868 | 10.112 | 10.349 | 10.310 |
| 34.0 | 10.92 | 10.79 | 10.97 | 10.91 |
| 35.0 | 11.69 | 11.46 | 11.56 | 11.48 |
| 37.7 | 13.41 | 13.52 | 13.23 | 13.09 |

The several equations given below serve to reproduce the observed values of A, with probable errors for each observation, as follows:

For formula A, probable error $= \pm 0.087$
" " B, " " $= \pm 0.107$
" " C, " " $= \pm 0.112$

The points whose coördinates are $t$ and $a$, after being platted upon engineer's profile paper, were found by a method of approximation to lie near the curve

$$(7.5 + a)(62.5 - t) = 521.4^1$$

or

$$a = \frac{521.4}{62.5 - t} - 7.5 \qquad (A)$$

But since it is usual, in similar investigations, to use equations of the form

$$a = A + Bt + Ct^2 + \text{etc.},$$

I selected seven points lying near the smooth curve of the diagram, and by the method of least squares obtained the equation

$$a = 1.55 - 0.022t + 0.0088t^2 \qquad (B)$$

The coefficient $B$ of the empirical formula can be made equal to zero, without greatly affecting the form of the curve within the range observed. The most probable equation of two constants is

$$a = 1.436 + 0.0082t^2 \qquad (C)$$

These constants are deduced from all the observations of Series III., by the method of least squares; but the refinement of assigning a particular weight to each observation was omitted.

The curves represented by these three equations lie quite close together, as shown by the calculated values given in the table. A closer agreement with the observations would have been obtained by an equation of the form

$$a = A + Ct^2 + Dt^4.$$

Each curve becomes rapidly steeper as $t$ is increased. It is impossible at present to determine the precise form of the equation representing the relationship under discussion; for even within the limited range of 34.1° there were special sources of error affecting the two extremes of the series; yet it may be safely assumed that

[1] As stated in my preliminary note, this Journal, 3, 203.

*the increase of speed is approximately as the second power of the temperature*[1] as represented in eq. (*C*).

If we try to picture the progress of the reaction in dilute aqueous solution, we realize that the molecules of the two "active" substances are greatly retarded in their chemical interchange by the vastly greater number of "inactive" water molecules. If the water were physically as well as chemically inactive, the chemical change would soon become impossible, because the separated ether and soda molecules could not come within the sphere of each other's influence. It can scarcely be doubted that the speed of chemical action increases with the temperature for a double reason; first, because the *liquid diffusion* is thereby increased by which the chemically active bodies are brought together, and secondly, by the increased *inter-atomic motion* within the reacting molecules, by which their sphere of mutual influence is enlarged. Weber's recent researches[2] on diffusion, as well as the older experiments of Eckhard,[3] show that *the increase in the coefficient of diffusion for dilute solutions is nearly proportional to the first power of the temperature.*

It may also be mentioned in this connection that the electrical conductivity of solutions (if not unusually viscous) is shown by Exner and Goldschmiedt[4] and by Kohlrausch[5] to vary far more nearly with the first power than the second power of the temperature.

To distinguish precisely between the two causes of increased speed of chemical action with higher temperatures, to show how much is due to more rapid diffusion, and how much must be attributed to the strictly chemical causes manifested within the molecules, will of course require more extended and accurate experimental data. It seems evident, however, that the foregoing determinations indicate that *an increase of temperature is accompanied by an increase of atomic motion within the several molecules of the fluid.*

Believing that the work done thus far has chiefly served to prepare the way for more accurate and extended investigation, with promise of fruitful results, I hope to continue this research as soon as circumstances will permit, with the aid of less active saponifiers.

NORTH BEND, OHIO, *July* 25, 1881.

[1] Hood suspected that the action of $KClO_3$ upon $FeSO_4$ varies as the square of the temperature.—Phil. Mag. [5] **6**, 383.

[2] Wied. Ann. Phys. **7**, 469, 536.

[3] Pogg. Ann. **128**, 61.

[4] Wied. Ann. Phys. **4**, 417; **6**, 73.

[5] Wied. Ann. Phys. **6**, 1, 145.

## XXIV.—SOME NEW COMPOUNDS OF PLATINUM.

By F. W. Clarke and Mary E. Owens.

The action of potassium cyanate upon the compounds of platinum seems never to have been systematically studied. We have begun an investigation upon the subject, and now present some of our earlier results.

When cold alcoholic solutions of platinum tetrachloride and potassium cyanate are mixed, a pale buff-yellow precipitate is thrown down. If the mixture is heated, this precipitate undergoes partial decomposition, and what is apparently metallic platinum separates out. By filtration, washing with alcohol, and drying at ordinary temperatures over sulphuric acid, the precipitate may be obtained in a stable condition. It is soluble in water, but completely insoluble in alcohol, and its aqueous solution decomposes upon boiling. Analysis gives the following percentages, which agree with the novel formula $K_2PtCl_3(CNO).H_2O$.

| | Found. | | | Theoretical. |
|---|---|---|---|---|
| Pt | 38.41 | 38.44 | 38.6 | 38.19 |
| Cl | 34.79 | 35.19 | 34.74 | 34.77 |
| $K_2$ | 15.08 | 14.53 | 14.67 | 15.28 |
| C | 2.27 | .... | ... | 2.35 |
| $H_2O$ | 3.76 | 3.22 | ... | 3.52 |

For want of sufficient material, nitrogen was not estimated. The presence of the cyanic molecule in the compound is, however, unquestionable.

By the action of potassium cyanate upon the green salt of Magnus, $PtN_2H_6Cl_2$, new compounds are formed, apparently of great complexity. The Magnus salt was prepared by the addition of a solution of potassium chloroplatinite to aqueous ammonia. A pure product is thus almost immediately formed, whereas the methods hitherto laid down for the preparation of this body gave us very unsatisfactory results. The Magnus salt dissolves readily in a hot aqueous solution of the cyanate, yielding a dark brown solution; which, concentrated over the water-bath to its crystallizing point, deposits pale yellow needles. From the mother liquor, beautiful clusters of brown needles were obtained. The yellow salt contained platinum, potassium, ammonia, water, and

carbon; the platinum amounting to 43.93 per cent. In the brown crystals, ammonia, platinum, and chlorine were found. Both salts are to be systematically investigated.

One other new salt was incidentally obtained by us. The well known potassium sulphocyanoplatinate is prepared by the action of potassium sulphocyanate upon the chloroplatinate. Happening to have a quantity of the strychnia chloroplatinate on hand, we dissolved it in potassium sulphocyanate. The blood-red solution, which was obtained after short boiling, deposited on cooling a brilliant red crystalline precipitate. This proved to be the strychnia salt analogous to the potassium sulphocyanoplatinate, and gave percentages of platinum and sulphur agreeing with the formula $2(C_{21}H_{22}N_2O_2)H_2PtCy_6S_6$.

| | Found. | Theoret cal. |
|---|---|---|
| Pt | 14.12 | 14.49 |
| S | 13.76 | 14.01 |

Doubtless other sulphocyanoplatinates of alkaloids may be easily obtained.

The investigation of the products resulting from the action of cyanates upon platinamines is to be followed up at an early day. The whole subject of the reactions between cyanates and salts of the various metallamines and metallammoniums bids fair to yield results of considerable interest.

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## XXV.—ON SOME SALTS OF CHROMIUM AND MERCURY.

By F. W. Clarke and David Stern.

The double salts which mercuric chloride and mercuric cyanide form with certain alkaline chromates have long been known. The following have been described.

| | | |
|---|---|---|
| 1. | $(NH_4)_2Cr_2O_7.HgCl_2.H_2O$ | Darby, Richmond and Abel. |
| 2. | $3(NH_4)_2Cr_2O_7.HgCl_2$ | Richmond and Abel. |
| 3. | $K_2Cr_2O_7.HgCl_2$ | Millon. Darby. |
| 4. | $K_2CrO_4.2HgCl_2$ | Darby. |
| 5. | $K_2CrO_4.2HgCy_2$ | Poggiale. Caillot and Podevin. |
| 6. | $Ag_2Cr_2O_7.2HgCy_2$. | Darby. |

These salts we have subjected to a reëxamination, and we have sought to prepare others of the same series.

The first of the foregoing compounds was our chief object of study. Our results concerning the others may be stated briefly. Salts numbered 3 and 4 we prepared, but found them difficult to purify. To number 5, Darby and Rammelsberg both assign the formula $2K_2CrO_4.3HgCy_2$. This formula requires 9.09 per cent. of chromium, while the one given above corresponds to 7.45 per cent. We found 7.62 per cent., thus confirming the simpler formula. The salt numbered 6 we found easy to prepare, and we verified its composition. We tried also to obtain a corresponding salt containing thallium in place of silver, but only thallium dichromate was deposited. We also attempted to produce double salts of mercuric cyanide with ammonium chromate, ammonium dichromate, and potassium dichromate, and of mercuric chloride with ammonium chromate; but in none of these experiments were we successful.

The salt numbered 1, and given by Richmond and Abel the formula $(NH_4)_2Cr_2O_7.HgCl_2.H_2O$, is easily prepared. The salts represented in it are dissolved together in equivalent proportions, and from the concentrated solution the double compound is deposited in large, showy crystals. As obtained by us, however, it was anhydrous. As formulated by Richmond and Abel, it should contain 3.33 per cent. of water; but, as obtained by us, it lost no weight even after long heating at 150°. An estimation of chromium gave us 19.80 per cent. The theoretical percentage for an anhydrous salt is 19.88; for a monohydrated compound, 19.22.

From the mother liquor of the foregoing compound Richmond and Abel obtained the salt which we have numbered 2. This body we did not obtain. Various attempts were made to prepare it, but all were unsuccessful. Several crops of the original salt were deposited in succession, and finally some orange-red laminae were secured which were neither ammonium dichromate nor either of the double salts above referred to. They were, however, contaminated with mercuric chloride, and were not in sufficient quantity for purification and complete analysis. To the mother liquor from them ammonia was added. A heavy dirty yellow precipitate was at first formed, which redissolved in an excess of the precipitant. The solution thus obtained deposited dark clove-brown granular crystals, also in quantity insufficient for thorough analysis. They

were insoluble in cold water, but boiling water decomposed them, with separation of a yellow basic chromate of mercury. At 150° the crystals lost 1.68 per cent. of their weight, and at 200° 16.66 per cent. 17.04 per cent. of chromium, 8.89 of ammonia, and 43.70 of mercury were found in them, but no chlorine. From this meagre evidence we can deduce no probable formula; but we suspect the body to be a double salt of an ammonium chromate, with a chromate of one of the mercurammonium bases.

Upon adding a caustic alkali to a solution of the salt $(NH_4)_2Cr_2O_7.HgCl_2$, a yellow precipitate was thrown down, which proved to be a basic chromate of mercury. From hot solutions precipitates were formed of variable composition; but from cold solutions a compound was deposited consisting definitely of the salt $7HgO.2CrO_3$. Our analytical results were as follows, in percentages:

| | Ammonia ppt. | Soda ppt. | | Theoretical. |
|---|---|---|---|---|
| Cr | 6.08 | 6.09 | 6.14 | 6.07 |
| Hg | 80.74 | 81.41 | ... | 81.77 |

The same compound was partially studied in this laboratory two years ago by Miss Helena Stallo, but her results were not published. She obtained the following percentages of chromium:

| | $NH_4OH$ ppt. | NaOH ppt. | KOH ppt. |
|---|---|---|---|
| Cr | 6.09 | 5.96 | 6.07 |

These figures are interesting, inasmuch as the same compound was prepared by a different process by Geuther,[1] whose results were afterwards discredited by Freese.[2] According to the latter chemist there is probably but one basic mercuric chromate, viz., the tribasic compound $3HgO.CrO_3$. Our results confirm Geuther's, and from another line of investigation. The following equation represents the formation of the salt:

$$7(Am_2Cr_2O_7.HgCl_2)+24NaOH$$
$$=12Na_2CrO_4+14AmCl+7HgO.2CrO_3+12H_2O.$$

The addition of a solution of borax to a solution of the salt $Am_2Cr_2O_7.HgCl_2$ also produces a yellow precipitate. This product agrees fairly with the formula $4HgO.CrO_3$, as the subjoined figures show:

| | Found. | Theoretical. |
|---|---|---|
| Cr | 5.10 | 5.38 |
| Hg | 82.34 | 82.88 |

[1] Ann. Chem. Pharm. **106**, 244.

[2] Poggend. Annal. **140**, 76.

The filtrate from this precipitate, upon concentration, gave white scaly crystals, which proved upon analysis to be boric acid. Hence, the following equation is probable:

$$4(Am_2Cr_2O_7.HgCl_2)+7Na_2B_4O_7 = 7Na_2CrO_4+8AmCl+4HgO.CrO_3+14B_2O_3.$$

If, instead of borax, hydro-disodic phosphate be used for a precipitant, still another basic chromate is thrown down. It agrees approximately with the formula, $6HgO.CrO_3$.

| | Found. | | Theoretical. |
|---|---|---|---|
| Cr | 4.07 | 4.04 | 3.79 |
| Hg | 86.43 | ... | 85.96 |

This corresponds to the subjoined equation,—

$$6(Am_2Cr_2O_7.HgCl_2)+11Na_2HPO_4 = 11Na_2CrO_4+12AmCl+6HgO.CrO_3+11HPO_3.$$

The last term in the equation was not verified, but it is suggested by the actual formation of boric acid in the previous case.

In conclusion, our results establish the existence of the basic chromate, $7HgO.2CrO_3$, and render the existence of two other basic chromates of mercury highly probable. All three are thrown down definitely from cold solutions, and all are more or less changed by boiling.

## THE ELECTROLYTIC DETERMINATION OF COPPER AND THE FORMATION AND COMPOSITION OF SO-CALLED ALLOTROPIC COPPER.[1]

By J. B. Mackintosh.

The quantitative determination of copper by means of electrodeposition offers so many advantages, that it is to be preferred, when properly executed, to all other methods for ease and accuracy. The object of the present paper is to give the results of a number

[1] Read at the Virginia meeting of the American Institute of Mining Engineers.

of experiments made during the past few months, and to indicate some sources of error which must be avoided in order to attain the necessary accuracy.

In 1867, C. Luckow, in competition for a prize offered by the directors of the Mansfield Copper Works, submitted the following process for the estimation of copper, and received, not indeed the prize, but an honorable mention for the simplicity, cheapness, and elegance of his process. He directs that the copper and the accompanying metals be obtained in the form of nitrates in solution in dilute nitric acid containing not more than 0.100 gram of the pure acid in each cubic centimeter; to this solution is added a few drops of a solution of an organic acid, such as tartaric or oxalic, and the copper is then precipitated on platinum in the usual manner. It is claimed that the copper is obtained in beautiful reguline form, while zinc, iron, and nickel are not precipitated at all.

In adapting this method to the analysis of copper alloys, I dissolved the alloy in nitric acid, evaporated the solution to dryness to get rid of the excess of acid, dissolved the residue in water with the addition of a few drops of nitric acid, to dissolve the basic nitrate of copper formed, and to this solution added four or five drops of a concentrated solution of citric acid. This solution was then precipitated in a platinum dish with a current from two Bunsen cells of about one quart capacity. In precipitating several samples at once I have it arranged so that the whole current traverses the row of dishes, the negative pole of each set being connected with the positive pole of the next succeeding one. In this case, if $n$ be the number of dishes, then $n+1$ is the number of battery cells of that size used.

Some of the results obtained by this method, and on duplicate portions by precipitation from sulphuric acid solution, are as follows:

| | Sulphuric Acid. | Nitric+Citric Acid. | Error. |
|---|---|---|---|
| 1 gram pig copper | 98.00 | 99.42 | +1.42 |
| " " | 99.80 | 101.22 | +1.42 |
| " " | 98.92 | 100.41 | +1.49 |
| " " | 98.72 | 100.27 | +1.55 |
| " " | 99.60 | 100.45 | +0.85 |
| 1 gram brass | 65.83 | 66.93 | +1.10 |
| " " | 65.83 | 66.58 | +0.75 |

In only one case was a smaller percentage obtained by the use of this method, and in that case the precipitation of the copper was not complete. In many cases, also, in which the amount of error was less than one per cent., small quantities of copper escaped precipitation and were afterwards found in the solution.

The metallic precipitate thus produced is of a much lighter color than ordinary copper from the electrolysis of the sulphate solution, but it is, as Luckow says, deposited in beautiful reguline form, which, however, hardly compensates for the error of perhaps one per cent. or more which we see is, as a general rule, the case.

Moreover, if the current is strong, after all the copper has been thrown down, zinc will be deposited on the surface of the copper, as a dark coating, which may be recognized as such by dissolving in dilute sulphuric acid and applying appropriate tests.

In the presence of the organic acid the formation of peroxide of lead on the positive pole is hindered, and in its absence it is very difficult to precipitate the whole of the copper from the solution.

In order to obtain sufficient material for analysis, to ascertain the cause of the excess in weight, the precipitation of the copper was made on a piece of platinum foil. On attempting to strip the deposit from the foil, I found that it was extremely brittle and scaled off easily; so brittle, indeed, that it could be reduced to an impalpable powder in an agate mortar with very little trouble. This agrees exactly with the description of the allotropic copper of M. P. Schützenberger, which was published in *Comptes Rendus*, vol. 86, part 2. M. Schützenberger obtained the material he describes by the electrolysis of a ten per cent. solution of the neutral acetate of copper. He found that the product contained from five to ten per cent. of suboxide of copper. In the material which I prepared from the nitric and citric acid solution I did not find *any* suboxide of copper; on the other hand, both carbon and hydrogen have been detected and estimated. These latter were determined by combustion of the finely divided sample in oxygen; the method used to estimate the suboxide of copper was that of Hampe.[1] However, oxygen is present, though, as this test shows, not as cuprous oxide.

The results of the analyses of several samples, prepared at different times, are given below. The determinations were all made on the amount of one grain:

[1] Zeitschrift für analytische Chemie, 1878, 127.

| | a | b | c | d | e | f | g | h |
|---|---|---|---|---|---|---|---|---|
| Carbonic acid..... | .0273 | .0316 | .0350 | .0344 | .0322 | .0324 | .0346 | .0283 |
| Equivalent to Carbon..... | **.00744** | **.00862** | **.00954** | **.00938** | **.0088** | **.0088** | **.0094** | **.00771** |
| Water..... | .0094 | .0108 | .0089 | .0094 | .0054 | .0045 | .0074 | .0054 |
| Equivalent to hydrogen..... | **.00104** | **.00120** | **.00100** | **.00104** | **.0006** | **.0005** | **.00082** | **.0006** |
| Ratio of carbon to hydrogen. | 7.15 | 7.18 | 9.54 | 9.0 | 14.6 | 17.6 | 11.46 | 12.42 |
| Copper..... | | | **.9683** | **.9687** | | | | |
| Total..... | | | **.97884** | **.97912** | | | | |

The results which are bracketed are from duplicate analyses. These samples were all prepared from the nitric and citric acid solution. *a*, *b*, and *c d* were prepared simultaneously, the solution of *b* containing a little more citric acid than that of *a*, and *c d* more than either. The samples *e*, *f*, *g*, and *h* were heated to about 100° C. for fifteen minutes before being introduced into the combustion tube, and the samples *c*, *d*, *e*, and *f* were the same. The results given under *h* are low, probably due to imperfect oxidation.

It will be seen that there is a deficiency of .02116 and .02088 respectively in the total of the duplicate analyses *c* and *d*. The precaution was taken in one case, of passing the products of the combustion over a red hot layer of oxide of copper, to make sure that no hydrocarbon was distilled out by the gradually increasing heat and so escaped oxidation. The results in this case, however, differed in no material manner from those already obtained. We must, therefore, conclude that this deficiency must consist either of *oxygen* or *nitrogen*, or of a mixture of both. I have already mentioned that there is no oxygen in the form of cuprous oxide present, so that it must, if present, be combined in some other form. The following synthetical experiments seemed to indicate that *nitrogen* was also an essential constituent.

These experiments were conducted as follows: Solutions were prepared of nitrate and of sulphate of copper; to these solutions were added respectively, citric acid, tartaric acid, and alcohol. All three of the solutions of the nitrate furnished the brittle deposit,

while all three of the sulphate solutions gave a tough deposit of apparently ordinary electrotype copper. The amount of copper was determined in 1.0008 gram of the precipitate from the sulphate solution containing alcohol, and found to be 0.9991. This difference is probably due to impurities in the copper, which was prepared in the first place from the commercial sulphate, which contained lead and other impurities.

During the electrolysis of the nitrate solutions containing citric acid, a very strong odor of hydrocyanic acid was perceptible.

If an insufficient amount of organic matter be added, the precipitated copper obtained is not brittle, but it nevertheless contains carbon and hydrogen and gives a total result less than 100 per cent. This is due to admixture of ordinary copper. It is not possible to divide such a precipitate sufficiently finely to ensure perfect oxidation.

The amount of nitrogen present in the nitric-citric precipitated copper, was determined by heating the finely pulverized sample in a vacuum and collecting the gases evolved. The products thus obtained were hydrogen, carbonic acid, and nitrogen. When heated in an atmosphere of oxygen, insufficient to completely oxidize the copper, the products were water, carbonic acid, and nitrogen. Although in this case it was probable that an excess of oxygen would be present, yet the analytical results showed the absence of that gas in any appreciable quantity.

The volumes given are those of the dry gas at 0° C. and 760 mm.

| 1 gram heated *in vacuo*. | | ½ gram in Oxygen. | 1.15 gram in Oxygen. |
|---|---|---|---|
| Gas obtained, | 9.95 cc. | 8.23 cc. | 17.52 cc. |
| $CO_2$ absorbed by KOH, | 4.72 " | 7.35 " | 15.70 " |
| Gas not $CO_2$, | 5.23 " | 0.88 | 1.82 " |
| Ogygen added, | 7.77 " | These residues treated with moist phosphorus to absorb oxygen, and then with KOH, did not change, proving the absence of oxygen. | |
| | 13.00 " | | |
| Volume after explosion, | 7.44 " | | |
| Loss—Water, | 5.56 " | The circumstances of formation were such as to preclude the existence of hydrogen, therefore these residues must be nitrogen. | |
| No $CO_2$ formed: *Hydrogen*, | 3.71 " | | |
| Residue: *Nitrogen*, | 1.52 " | | |

The percentage results in the foregoing three cases are respectively for nitrogen: 0.191, 0.221, 0.199; and in the two last for carbon: 0.792, 0.736. The ratio of $\frac{C}{N}$ being 3.6 and 3.7.

One sample of the product, made with tartaric acid, weighing two grams, was also analyzed for nitrogen, and one cubic centimeter of dry nitrogen at 0° C. and 760 mm. obtained. It is difficult when working on such small quantities of gas to obtain very accurate results.

Some of the allotropic copper prepared from the chemically pure acetate according to M. Schützenberger's directions, and which therefore could not contain nitrogen, and also some prepared from an acetate of copper containing nitrate of soda, were compared and analyzed. The material thus obtained was apparently the same in both cases, and differed considerably in some of its properties from the nitric-citric acid solution precipitate. In appearance, brittleness, and composition there was no essential difference, but it was very unstable and liable to oxidize, in fact it was not possible to preserve it of constant composition in the air, while the nitric-citric precipitate can be preserved indefinitely without change.

Two samples of 1.0014 and 1.0004 grams respectively were weighed out. The first was heated for about fifteen minutes to 100° C. in an air-bath; on cooling and weighing it had gained 0.0215 gram. The second sample was exposed to the air at the ordinary temperature for two hours and three-quarters, at the end of that time it had gained 0.0225 gram; it was then heated to 100° C. for fifteen minutes, when it lost 0.0020 gram, giving a net gain of 0.0205 gram.

The amounts of carbon and hydrogen were determined in the second sample of the material from the acetate solution containing nitrate of soda, and in two samples from the chemically pure acetate preparation.

| | $Cu(C_2H_3O_2)_2 + NaNO_3$ | $Cu(C_2H_3O_2)_2$ | |
|---|---|---|---|
| Amount taken, | 1.004 gram[1] | 1 gram | 1 gram |
| $CO_2$ found | .0145 | .0175 | .0154 |
| Equivalent to C | .00395 | .00477 | .0042 |
| $H_2O$ found | .0081 | .0092 | .0081 |
| Equivalent to H | .0009 | .00102 | .0009 |
| Ratio, C : H | 4.4 | 4.676 | 4.666 |

The cause of the rapid oxidation of these samples seems to be that the deposit is very porous, while that from nitric solutions is very dense.

[1] Oxidized by exposure to air and heating in air-bath before combustion.

M. Schützenberger mentions that he had at one time a considerable quantity of this allotropic copper *(sic)* reduced to powder and dried in a vacuum, which at the moment when air was admitted to it was transformed to ordinary copper, attended by a considerable evolution of heat. The amount of oxygen he found was not altered by this occurrence.

To account for this phenomenon he frames the theory that the allotropic copper corresponds to cuprous copper, and that the molecular change to cupric copper is accompanied by the development of heat. But we can easily see how liable to spontaneous oxidation a large quantity of such finely divided material would be when it contains both carbon and hydrogen in a weak state of combination, and it is unnecessary to suppose the existence of another form of metallic copper to account for the phenomena noticed.

The practical conclusions to be drawn from these results are, that some organic matters, and in all probability all, in the presence of nitric acid in the copper solution undergoing electrolysis, cause erroneous results; that from a nitric acid solution, with no organic matter, it is extremely difficult to separate all the copper; and that the old method of electrolysis from the sulphate is the best.

HOBOKEN, N. J.

## REVIEWS AND REPORTS.

### REPORT ON PROGRESS IN PHYSIOLOGICAL CHEMISTRY.

### GASTRIC DIGESTION AND THE PRODUCTS FORMED.

*Forms in which Pepsin occurs.*—Recent facts lead to the opinion that the ferment pepsin contained in the mucous membrane of the stomach exists there in two distinct forms: the one readily soluble, the other slowly and with difficulty. Thus Brücke[1] remarks that a mucous membrane which has been thoroughly extracted with very dilute hydrochloric acid still yields pepsin again and again at each fresh extraction. Likewise Schiff[2] has found that a hydrochloric acid infusion of the mucous membrane when allowed to stand some weeks, grows richer and richer in pepsin, especially when a large quantity of fluid has been employed. Again, the investigations of

[1] Vorlesungen, 1 Auf. 287, 1874. [2] Arch. d. sc. phys. et nat. 1877.

Ebstein and Grützner[1] have shown conclusively that that portion of the pepsin difficultly soluble does not exist free in the glands, but is united to another substance, probably an albuminate, a pepsinogen compound which Schiff has named *propepsin.*

The following are a few of the facts which tend to further support the idea of a pepsinogen substance.[2] If a portion of dried and finely divided mucous membrane (from cardiac or pyloric region) is laid in glycerin, a glycerin extract is obtained which contains less pepsin than when the glycerin extraction is preceded by a preliminary treatment with 1 per cent. sodium chloride solution or .2 per cent. hydrochloric acid. The reason of this, as Heidenhain says, is not that the glycerin possesses only a limited solubility for pepsin, for the content of pepsin increases with the quantity of mucous membrane employed, but that only one part of the pepsin is originally soluble in glycerin, while the other is rendered soluble by the action of sodium chloride or hydrochloric acid, both of which presumably cause the pepsin to split off from the body with which it was originally combined; the salt less, the acid more completely. Again, if an aqueous solution of the mucous membrane is evaporated to dryness at 40° C., a residue is obtained which is completely soluble in glycerin. This solution, however, is poorer in pepsin than a solution prepared by dissolving the residue in an equal quantity of dilute hydrochloric acid. It is therefore obvious that the residue left by the evaporation of the aqueous extract contains besides free pepsin a substance which yields pepsin or from which pepsin can be liberated, not however by simple solution in glycerin, but by the action of a very dilute hydrochloric acid. According to Schiff the breaking up of the pepsinogen substance is hindered by a solution of sodium carbonate. Doubtless pepsinogen is an intermediate product in the metamorphosis of the protoplasm of the secreting cell. Being difficultly soluble it may serve the purpose of a reserve fund, from which at any time pepsin can be liberated by the acid of the gastric juice.

*Place where Pepsin occurs.*—In 1839 Wassmann made the discovery that the glands of the pyloric portion of the stomach of swine differed from the glands of the cardiac region, and since that time until recently the seat of the pepsin formation was supposed to be wholly in the glands of the cardiac portion of the stomach. In 1870–1874 Ebstein and Grützner[3] proved conclusively the presence of pepsin in the pyloric membrane, and from its constant presence they concluded that the glands of the pyloric possessed, in common with the glands of the cardiac, the function of secreting pepsin. Before this, Wassmann and other physiologists had detected pepsin in the pyloric membrane, but they in common with von Wittich and others held that it was present there by infiltration from the cardiac, and in support of this theory Wassmann claimed

[1] Arch. f. d. ges. Physiol. **8**, 122, 1874.
[2] Heidenhain in Hermann's Handbuch d. Physiologie, Band 5, 1 Theil. 129.
[3] Arch. f. d. ges. Physiol. **3**, 565, 1870. Ibid. **6**, 1, 1872; Ibid. **8**, 122 and 617, 1874.

that the membrane of the pyloric could be freed entirely from its content of pepsin by repeated washing with water. Friedinger[1] however was not able to remove the pepsin from the pyloric membrane even by 24 hours' washing in running water. About the same time Fick[2] found by artificial digestions with different portions of the stomach mucosa, that the mucous membrane of the pyloric region possessed about one-half the digestive power of the mucous membrane from the cardiac. In 1879 Langendorff[3] made the observation that the *port. pylorica* in an ox embryo contained pepsin, and this at a stage of development when the stomach itself contained an alkaline fluid perfectly free from pepsin, thus showing without a shadow of doubt that the ferment may be formed in the pyloric membrane.

Finally, Klemensiewicz,[4] and later, Heidenhain,[5] by examining the secretion from the isolated pyloric portion of the stomach, proved conclusively the presence of pepsin, while at the same time Heidenhain, more successful in his method of experimentation, succeeded in obtaining from his artificially prepared "pylorous blind sack" an alkaline secretion rich in pepsin for a period of five months, thus establishing on a firm basis the theory of a pepsin formation in the pyloric. Within the last ten years, observations have been multiplied which show a widespread distribution of pepsin, or at least a pepsin-like substance, in animal tissues and fluids. As far back as 1861 Brücke[6] found in urine and in muscle substance, traces of a body which with properly diluted HCl would dissolve fibrin. More recently Kühne[7] has found a similar substance in the mucous membrane of the intestines from dogs and swine, in intestinal juice, in lymphe, dog's blood, brain, and in the lungs, while Munk[8] has found it in human mixed saliva. Naturally the quantities found are exceedingly minute, but still in sufficient amount to identify the substance as a body similar to pepsin in its most important property of dissolving and digesting fibrin. Recent investigations of Krukenberg[9] have likewise shown a widespread distribution of both pepsin and trypsin-like ferments among many invertebrates; thus the secretion from the liver of various crustaceans such as *Homarus vulgaris* showed strong digestive action on fibrin in both acid and alkaline solutions. The same investigator also found a peptic ferment present in the yolk from hen's eggs.

*Origin of the Pepsin and free Acid in the Stomach.*—In the cardiac glands of the stomach the "Belegzellen" or ovoid cells are supposed to produce the acid, while the "Hauptzellen" or central cells produce the pepsin of gastric juice. The great similarity of

[1] Sitzgsber. d. Wien. Acad. **64**, 5.
[2] Würzburger Vehr. N. F. **2**, 61.
[3] Arch. f. Anat. u. Physiol. 1879, 102.
[4] Sitzgsber. d. Wiener Acad. **3**, Abth. 1875.
[5] Arch. f. d. ges. Physiol. **18**, 169. Ibid. **19**, 154.
[6] Sitzgsber. d. Wiener Acad. Math-naturwiss. Cl. **43**, 618.
[7] Verh. d. naturhist-med. Ver. zu Heidelberg, **2**, 1.
[8] Verh. d. Physiol. Ges. zu Berlin 1876, 24th Nov.
[9] Untersuchungen aus Physiolog. Institute, Heidelberg, **2**, 261–273.

the central cells of the cardiac with the cells of the pyloric was commented on long ago by Ebstein, and later when Heidenhain discovered the formation of pepsin by the pyloric cells he was struck with the similarity of the two, and immediately advanced the theory of a like function for the two kinds of cells. This theory was based particularly on the fact[1] that if a small piece of freshly isolated cardiac gland is placed in a drop of dilute HCl under the microscope and heated to 40° C., the central cells quickly break up and are soon almost entirely dissolved, excepting the shrunken up nucleus. The ovoid cells, however, simply appear swollen and more transparent. Naturally under the above circumstances those cells which contain the ferment will dissolve most rapidly, and it was on this fact that the theory of a pepsin formation in the central cells was originally founded. Again, Heidenhain[2] found that a hydrochloric acid infusion of the lower half of the cardiac glands, in which the proportion of central cells to ovoid cells is greater than in the upper half, was possessed of far greater digestive power than an infusion of the upper half of the glands. Among many other facts which point to the same conclusion we may mention the observations of Sewall,[3] who found in studying the development of the cardiac glands in the embryo of sheep, that the ovoid cells appeared first, and then later the central cells, while the presence of pepsin in the mucous membrane could be detected first, only on the appearance of the latter cells. As is now well known the central cells of the cardiac and the cells of the pylorus differ somewhat both in chemical composition and in form, in the hunger period, from that which they possess in the period of digestion. Thus in the condition of hunger the central cells of the cardiac in an alcohol preparation, examined in glycerin are seen to be large, transparent, and with the exception of the nucleus, very faintly or not at all colored by carmine or aniline blue, while at the end of digestion the cells are very much contracted, turbid with small particles, and capable of being thoroughly stained with carmine. Presumably then the material from which the pepsin or its antecedent propepsin is formed in the central cells of the cardiac or the cells of the pylorus is the albuminous matter of the protoplasm. Thus, if the cells have taken up considerable albuminous matter, or in other words are rich in protoplasm, as in the 8th or 10th hour of digestion, then the cells in an alcohol preparation are very turbid and take on a deep color with carmine, while during the hunger period the albuminous protoplasm is in great part gradually changed into the ferment or the pepsinogen antecedent, when the cells then become clearer and refuse to hold the coloring matter. In the words of Heidenhain, "when food is taken the secretory activity of the stomach commences, by means of which two processes standing to each other in the closest relationship, proceed

[1] See Heidenhain's description in Arch. f. microsc. Anat. **6**, 400.
[2] *Loc. cit.*
[3] Jour. of Physiol. **1**, 320.

hand in hand: the conversion of the pepsinogen substance into pepsin and the secretion of the latter on the one hand, the taking up of new albuminates, and thereby increasing the amount of protoplasm for the purpose of forming new ferment, on the other."

The formation of acid in the stomach is to be looked for wholly, without question, in the cardiac portion, and the cells which secrete it are undoubtedly the large ovoid cells. The acidity of gastric juice was ascribed by Prout to free hydrochloric acid in 1824. Later many investigators denied the presence of free HCl, and in 1840–1850 many prominent authorities, as Lehmann, Lassaigne and others, looked upon lactic acid as the principal acid of gastric juice, and Lehmann in particular accounted for the presence of free HCl in the last portions of the distillation fluid, obtained in distilling gastric juice, by the decomposition of calcium chloride by concentrated lactic acid. Later Lehmann succeeded in obtaining from the concentrated gastric juice of 20 dogs free lactic acid in sufficient quantity to form a crystalline salt for analysis. Blondlot believed that the acidity of gastric juice was due to acid calcium phosphate, and he finally adopted the view which at one time was common, that NaCl was decomposed in the walls of the stomach into NaOH and HCl, the acid giving with the calcium phosphate of blood an acid phosphate, together with a trace of free HCl and $H_3PO_4$, to which latter fact was due the solvent action of gastric juice on calcium carbonate; a fact which had long been quoted as proof of the presence of free acid. To the work of Carl Schmidt[1] however is due a true understanding of the acidity of gastric juice; he found as a result of 18 analyses that the pure gastric juice of carnivorous animals contained only free HCl, and no trace of lactic or acetic acid, while the juice of herbivorous animals contained besides HCl small quantities of lactic acid, which, however, had its origin probably in the starchy constituents of food. Schmidt's conclusions have never been overthrown, and there is no doubt that the principal acid of gastric juice is HCl. The undoubted occasional presence of various organic acids affords no evidence of incorrectness in the above statement, as they would undoubtedly be liberated from their various combinations by the more powerful hydrochloric acid. It has been recently suggested by Richet[2] that the HCl does not exist in a completely free condition, and he quotes several facts which lead him to this view; the most important of which is that gastric juice does not invert cane sugar, while HCl of the same strength does. This statement, which has been extensively circulated, is without doubt incorrect, for Lenssen[3] has distinctly proved that the formation of glucose from saccharose is a delicate test for the presence of free acid, and that the quantity of sugar formed is a measure of the acidity. The strong mineral acids form much more reducible sugar in the same time

[1] Bidder and Schmidt, Verdauungssäfte 40–50.
[2] Jahresbericht d. Thierchemie, **8**, 239.
[3] Jour. f. prakt. Chemie, **88**, 321. Also Zeitschrift f. analyt. Chem. **14**, 306.

than the organic acids, and act very energetically even in the smallest quantities and at the ordinary temperature. Likewise Szabo[1] has shown that the inverting action of human gastric juice on cane sugar approximates much more closely in its intensity to HCl than to lactic acid, this being very apparent when the three are tested side by side. Richet[2] however considers that the acid of gastric juice is a combination of HCl with leucin, and that this latter body modifies the action of the acid. Still more recently Reinhard v. d. Velden[3] has communicated the results of experiments with human gastric juice which are so decisive as to convince him that HCl is not the primary free acid. He found in a large number of cases that gastric juice obtained by means of a stomach-pump from human stomachs during the first period of digestion, contained no free acid, although the juice was strongly acid. Edinger[4] likewise failed to find any free acid in the acid gastric juice of frogs. After a time, however, free HCl can be detected in the human gastric juice, the length of time varying from ¾ to 2 hours, being apparently dependent upon the kind of food taken.

Many theories have been devised to explain the formation of free HCl in the stomach. Heidenhain is of the opinion that the chloride of the blood is the material from which the HCl is formed, the separation taking place in the stomach glands. Thus, according to his view, the chloride passes into the mucous membrane by diffusion, for Grützner found it present there in quantities sufficient to be detected. He likewise found that the mucous membrane under those conditions in which it was richest in pepsin, contained a much larger quantity of chloride than when by vigorous secretion the content of pepsin had been diminished. Thus Heidenhain is of the opinion that it is the function of the secreting membrane to decompose the chlorides obtained from the blood in order to form HCl for the purposes of digestion; this particular secretory process being presumably the main function of the large ovoid cells. According to his views also the decomposition of the chloride does not at once take place, but an organic acid is first formed which causes the HCl to separate from the alkali. This view is based on Brücke's statement that the substance of the stomach, by digestion in a warm place, develops an organic acid, presumably lactic. Then, too, Maly,[5] as well as others, has furnished direct proof of the possibility of the decomposition of chlorides by lactic acid, for he found that a mixture of sodium chloride and dilute lactic acid to which considerable water had been added, gave in a short time free HCl.

The mother substances from which the acid gastric juice must originally be formed are the alkaline lymphe and blood, and in order to understand the formation of an acid secretion from such a source Buchheim[6] has suggested the possibility of the alkali salts of blood

[1] Jahresber. d. Thierchemie, **7**, 267.
[2] *Loc. cit.*
[3] Zeitschrift f. Physiolog. Chemie **3**, 205.
[4] Arch. f. microscop. Anat. **17**, 198.
[5] Ann. d. Chemie, **173**, 228.
[6] Pflüger's Archiv. **12**, 326.

behaving to albumin in the same manner as the salts of the heavy metals; thus when albumin is treated with $CuSO_4$, two new compounds are formed, a copper-albumin compound and a sulphuric acid-albumin compound. In an analogous manner sodium-albumin and hydrochloric acid-albumin might originate in the blood, the latter compound undergoing disassociation in the ovoid cells of the stomach. Recently Maly[1] has undertaken to explain the formation of HCl by a totally different method. It has long been known that a mixture of $NaH_2PO_4$ and NaCl or $CaCl_2$ gives an acid reaction with methylanilin violet, also that such a mixture in water yields by diffusion free HCl. It therefore seems probable that $NaH_2PO_4$ partially decomposes the chloride, acting towards it like a free acid. It is also a well-known fact that the ordinary disodium phosphate $Na_2HPO_4$ is changed into the monophosphate by the action of $CO_2$. Now, according to Maly, all the conditions are favorable for such a change as this to take place in the blood. In blood, both NaCl and $Na_2HPO_4$ are present, and in the presence of an excess of $CO_2$, $NaH_2PO_4$ is also to be found. By the reaction of these bodies small quantities of free HCl are formed, and then owing to its high rate of diffusion the free acid at once passes by osmosis into the glands of the stomach, thus making of these glands a simple diffusion apparatus instead of a secretory one. Again, Pribram[2] and others have called attention to the peculiar action of alkaline disodium phosphate upon calcium chloride, which also appears to be present in the serum of blood. The precipitate produced by the union of these two substances is not exactly $CaHPO_4$, but is richer in calcium, being probably a mixture of di- with some triphosphate, a small quantity of HCl being liberated, which can readily be detected in the filtrate by methylanilin violet. The change which may take place in the above reaction can be expressed as follows:

$$3CaCl_2+2Na_2HPO_4=Ca_3(PO_4)_2+4NaCl+2HCl.$$

That such a change as this actually does take place in the blood is of course wholly hypothetical.

R. H. CHITTENDEN.

(*To be continued.*)

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## REPORT ON ANALYTICAL CHEMISTRY.

(*Continued from p.* 231.)

OXYGEN.—*Absorption by pyrogallol in alkaline solution.*—Th. Weyl and X. Zeitler.[3] The object of the investigation was to determine the dependence of this absorption upon the quantity of pyrogallol and the concentration of the caustic potassa. The

[1] Zeitschrift f. Physiolog. Chemie, **1**, 174.
[2] Jahresber. d. Thierchemie, **1**, 107. Also **3**, 109.
[3] Liebig's Annalen, **205**, 255.

method of experimenting consisted in passing a carefully measured volume of air through an alkaline solution of pyrogallol, and in determining the unabsorbed oxygen by the method of Schützenberger. The best results were obtained by dissolving 0.25 gram of pyrogallol in 10 cc. of caustic potassa having a specific gravity of 1.05. In this solution the absorption of oxygen was nearly complete.

*Volumetric solution for the determination of superoxides and oxidizing substances.*—A. Terreil.[1] The solution is prepared by dissolving 100 grams of ferrous sulphate in 500 cc. of water, adding 200 grams of concentrated sulphuric acid and diluting to 1000 cc. After standardizing with permanganate of potassium, from 0.2 to 0.3 gram of the substance (very finely pulverized) is treated with from 30 to 50 cc. of the solution, and warmed if necessary. The excess of ferrous sulphate is then determined by means of permanganate of potassium. In this way the superoxides of hydrogen, barium and lead, the oxides of manganese, the hypochlorites, and the sesquioxides of nickel and cobalt can be determined with excellent results. When barium or lead is present it is well to add a few cc. of hydrochloric acid.

WATER.—*The free oxygen and organic matter contained in natural waters compared.*—Th. Weyl and X. Zeitler.[2] The question to be answered was: Do the free oxygen and organic matter of such waters bear any fixed relation to each other? Seven waters were examined. The oxygen was determined by the method of Schützenberger, the organic matter by the method of Kubel. In five of the waters the oxygen was found to diminish as the organic matter increased. In the other two—the worst examined, this was not the case. It was therefore concluded that the quantity of free oxygen contained in waters, as already noted by others, is no measure of their excellence. It was found, moreover, that the quantity contained by one and the same water is not at all constant.

J. C. Thresh[3] describes a convenient form of apparatus for collecting the gases dissolved in water.

*Determination of nitrates.*—M. W. Williams[4] has found that the method of Gladstone and Tribe, if properly applied, yields excellent results. It was noticed that the time required for the reduction of a given quantity of nitrates varied in different waters, even when the conditions under which the reaction took place were apparently identical. This led to the suspicion that the rate of reduction is influenced by the character of the other constituents, and the suspicion was verified by the results of a systematic investigation upon standard solutions of nitrate of potassium. Carbonic acid, calcium carbonate and sulphate, sodium chloride and phosphoric acid were found to accelerate the reduction, while sodium hydroxide and carbonate and caustic lime retard it. The experiments were,

[1] Bulletin de la Soc. Chim. **35**, 551.
[2] Zeitschrift für Physiolog. Chemie, **5**, 10.
[3] Journal Chem. Soc. 1881, 399.
[4] Journal Chem. Soc. 1881, 100.

for the most part, performed at a temperature of 24°. At lower temperatures the reaction proceeds more slowly. In order to study the progress of the reduction, the ammonia and the nitrites were determined at stated intervals—the former by titration with Nessler's solution, the latter by the method of Griess. The relative quantities of these compounds found at the different stages of the reaction seem to justify the conclusion that the reduction consists of two distinct steps: 1. The conversion of the nitrates into nitrites. 2. The conversion of the latter into ammonia; and that but little ammonia is formed until after all of the nitrate has been reduced to nitrite. Hence the absence of nitrite indicates that the conversion of nitrate into ammonia is complete. The directions for the determination of nitrates in natural waters are as follows: "Some strips of zinc-foil or very thin sheet zinc are placed in a wide-mouthed stoppered bottle and covered with a 3 per cent. solution of copper sulphate. When the zinc has acquired a sufficient coating of copper, the solution is poured off and the copper-coated zinc washed free from zinc sulphate and drained. A portion of the water to be analyzed is then poured in and the couple rinsed with it in order to displace the adhering distilled water. The couple is again drained, and finally the bottle is filled with the water to be analyzed, the stopper inserted, and the whole allowed to digest in a warm place until the reduction of the nitrates is completed. The water may then be found turbid with floating particles of oxide of zinc; to remove these, it is poured off into a stoppered bottle and left at rest until the turbidity has subsided. A measured portion of the clear supernatant fluid is then withdrawn, diluted to the necessary extent, and the ammonia in it titrated by Nessler's method." About one square decimeter of zinc should be used for every 200 cc. of water containing 5 parts or less of $NO_3$ in 100,000. When the water is richer in nitrates a larger surface should be employed. The reduction may be hastened by raising the temperature to 30°, or even 40°; by the partial saturation of the water with carbonic acid; or by the addition of a small quantity of sodium chloride.

Perkins[1] estimates the nitrates in water by placing 100 cc. of it in a platinum dish, inserting a spiral of magnesium, adding a little fused chloride of sodium, and allowing the whole to stand until the magnesium has dissolved. The ammonia is then distilled off and determined by Nessler's solution.

*Estimation of organic carbon and nitrogen simultaneously with the estimation of nitric acid.*—In order to avoid the use of sulphurous acid in the Frankland process, which is in many ways objectionable, M. W. Williams[2] first reduces the nitrates by means of the zinc-copper couple in the manner already described. After complete reduction has been effected, the ammonia, and indirectly

[1] Analyst, 1881, 58, taken from Berichte der deutsch. chem. Gesellschaft, **14**, 1586.
[2] Journal Chem Soc. 1881, 144.

the nitric acid, is determined in a measured portion of the solution which is withdrawn for the purpose, or in the distillate obtained by concentrating the portion which is to serve for the determination of organic carbon and nitrogen. During the distillation, which is continued until the volume of the liquid has been reduced to 200 cc. or even less, one or two drops of a concentrated solution of sodium carbonate, or a small fragment of calcium oxide, is added to insure the complete removal of ammonia. If calcium carbonate is in the meantime deposited upon the sides of the retort, it is decomposed by means of phosphoric acid or a small quantity of sulphurous acid, which at this stage of the process can do no harm. The solution is then brought into a smooth hemispherical dish and evaporated to dryness. The combustion of the residue is effected in the manner prescribed by Frankland.

CHLORINE.—*Estimation of chlorine, cyanogen and sulphocyanogen in the same solution.*—W. Borchers.[1] From 10 to 20 grams of the mixed salts are dissolved in water and diluted to one litre. A portion of this solution is measured off, and the quantity of a standard silver solution required to exactly precipitate all three of the substances determined. To another equal portion is added the same amount of the silver solution. The precipitate, still moist, is treated with nitric acid having a specific gravity of from 1.37 to 1.40 and boiled. The undissolved residue contains all of the chlorine as silver chloride. A determination of the sulphuric acid in the filtrate gives the amount of the sulpho-cyanogen originally present. The cyanogen is then indirectly determined by estimating the silver in the filtrate by Volhard's method, and subtracting from the amount found a quantity equivalent to the sulphocyanogen. If ferrocyanogen is also present, it is first removed by adding a ferric salt free from chlorine, after which the filtrate is treated in the manner described.

PHOSPHORUS.—*Determination of phosphoric acid in phosphates.*—A. Grupe and B. Tollens[2] have undertaken an investigation of the conduct of phosphates towards citrate of ammonium, in order to ascertain (1) the cause of the solvent action of the latter, and whether there is an essential difference in its conduct towards different phosphates; (2) whether the determination of phosphoric acid in citrate of ammonium solutions by direct precipitation with magnesia mixture (method of Petermann) is sufficiently exact. They conclude that the solvent action is due to the formation of phosphate of ammonium and citrate of calcium which dissolves in the excess of citrate of ammonium. And the following facts are cited to justify the conclusion: (1) if a solution of phosphate in citrate of ammonium is allowed to stand or is evaporated, citrate of calcium crystallizes out; (2) crystals having the same appearance form at once when a solution of citrate of ammonium is poured on an

[1] Repert. der analyt. Chemie, 1881, 130, taken from Berichte der deutsch. chem. Gesellschaft, **14**, 1587.
[2] Berichte d. deutsch. chem. Gesellschaft, **13**, 1267.

excess of the phosphate; (3) citrate of calcium dissolves easily in citrate of ammonium, and alcohol precipitates from such solutions a double citrate of calcium and ammonium. They find moreover that tricalcium phosphate ($Ca_3 2PO_4$) is also soluble to a considerable extent in citrate of ammonium, though much less so than the dicalcium salt ($CaHPO_4 2H_2O$); and conclude, therefore, that there is no essential difference in the conduct of the citrate towards the so-called insoluble and reverted or precipitated phosphates. They suggest that the difference in the solubility of the two kinds of phosphates may be due to differences in their physical conditions.

In regard to the second question, namely, whether the method of Petermann gives sufficiently accurate results, they state that if three times the calculated amount of magnesia mixture is added to the solution of phosphate in citrate of ammonia, the precipitation of the phosphoric acid is nearly complete; but the precipitate contains calcium, rendering its solution in hydrochloric acid and reprecipitation by ammonia necessary. If a still larger proportion of the magnesia mixture is added, the precipitation of the phosphoric acid is incomplete; but the precipitate contains calcium and an excess of magnesium. These errors may or may not compensate each other.

A. Herzfeld and G. Feuerlein,[1] on the other hand, believe that the solvent action of the citrate is due to the formation of phosphate of calcium ammonium ($NH_4CaPO_4$) which dissolves in the excess of citrate of ammonium. They observed, like Grupe and Tollens, that the precipitate obtained from citrate solutions of phosphate by magnesia mixture always contains calcium. At first they ascribed its presence to the absorption of carbonic anhydride from the air by the ammoniacal solution, but concluded that this could not be the case, having found that carbonic anhydride does not precipitate calcium from solutions of calcium citrate or phosphate in ammonium citrate. Neither is the calcium which is found in the precipitate, there in the form of citrate; for the authors were unable to detect the presence of orthophosphates in the ignited precipitate by means of the silver reaction. The precipitate after ignition contains only pyrophosphates, which could not be the case if it had previously contained either carbonate or citrate of calcium. The conclusion is, therefore, that the calcium is precipitated as phosphate of ammonium calcium ($NH_4CaPO_4$) when the strongly ammoniacal magnesia mixture is added; and the following facts are given as confirming this view: (1) If ammonia gas is conducted into a concentrated solution of ordinary phosphate of sodium, phosphate of ammonia sodium ($NH_4Na_2PO_4.12H_2O$) is precipitated; (2) if a sufficiently concentrated solution of dicalcium phosphate ($HCaPO_4.2H_2O$) in citrate of ammonium is treated in the same manner or with a concentrated solution of ammonia, phosphate of ammonium calcium ($NH_4CaPO_4.xH_2O$) is precipitated. The citrate of ammonium solution employed by the authors was not that recom-

[1] Zeitsch. für analyt. Chemie, 1881, 191.

mended by Petermann. It was neutral instead of alkaline, and had a specific gravity of 1.105 instead of 1.09.

Grupe and Tollens[1] reply that in the absence of any direct statement upon the subject it is impossible for them to know how Herzfeld and Feuerlein have applied the silver test to detect the presence of orthophosphates in the ignited precipitate, but their own experiments, made upon solutions of ortho- and pyrophosphates of sodium, show that the yellow color indicative of the presence of the former does not distinctly appear when the proportion of orthophosphate is less than 10 per cent. If the solution is warmed the test is more sensitive, especially at the moment when the alkaline reaction of the solution disappears. But the reaction is uncertain even in warmed solutions, and it could sometimes be obtained in solutions of pure pyrophosphate. Any reaction for orthophosphoric acid obtained by dissolving the ignited precipitate in nitric acid, neutralizing with ammonia and adding nitrate of silver, would be indecisive, because of the known tendency of pyrophosphoric acid in the presence of nitric to pass into orthophosphoric acid. The silver nitrate test is, however, very sensitive when the solid material is simply moistened with the nitrate. If the ignited precipitate in question is tested in this manner it becomes decidedly yellow, showing the presence of orthophosphate. The objections of Herzfeld and Feuerlein to the views of the authors are therefore not valid, so far as they are based on the supposed absence of orthophosphates from the precipitate after ignition. Finally, the fact that a precipitate consisting of ammonium calcium phosphate was obtained from the citrate solution in the manner described by Herzfeld and Feuerlein is no proof that such a compound existed in the solution previous to precipitation.

A. Koenig[2] calls attention to a very serious defect of citrate of ammonium as a solvent for reverted phosphates—namely, the fact that widely varying percentages of phosphoric acid are obtained when different weights of any given material are treated with the same amount of citrate. One gram of material treated according to Petermann's method yielded 30.08 per cent. of phosphoric acid, while two grams of the same material treated in the same manner with an equal amount of the citrate solution yielded only 25.12 per cent. In another case one-half gram gave 19.20 per cent. of phosphoric acid, while a whole gram gave only 12.80 per cent. The method of Fresenius, Neubauer and Luck gave similar and nearly equal differences. In order to obtain even relatively correct results it is necessary that the quantity of citrate used should always have a fixed proportion to the amount of reverted or precipitated phosphates to be dissolved, which is practically impossible. The point is an important one in view of the fact that there is lack of uniformity in the recommendations of different authorities as to the

[1] Berichte d. deutsch. chem. Gesellschaft, **14**, 1042.
[2] Zeitsch. für analyt. Chemie, 1881, 40.

quantity of material to be employed for the determination of phosphoric acid.

R. Hercher and P. Wagner[1] confirm the statement of Koenig, and observe, further, that the citrate is relatively less efficient as a solvent for so-called superphosphates than for precipitated phosphates, because of the presence in the former of large quantities of calcium sulphate, which must also be decomposed and dissolved at the expense of the citrate. They find, however, that this difficulty can be obviated by using ammonium oxalate in connection with the citrate. They conclude with reference to Petermann's method of direct precipitation from the citrate solution, that a portion of the phosphoric acid remains in solution, but if previous to solution it was in combination with non-volatile elements such as sodium, iron or calcium, especially the last, enough of these are precipitated to partially or even over-compensate for the unprecipitated phosphoric acid.

In view of the established objections to the use of citrate of ammonium in phosphate analyses: (1) that it dissolves tricalcium phosphate to a considerable extent; (2) that phosphoric acid cannot be completely precipitated from it by means of magnesia mixture; (3) that the precipitate nevertheless contains calcium and an excess of magnesium, though there is no certainty that their presence will compensate for the unprecipitated phosphoric acid; (4) that, in the presence of magnesium, the phosphate of ammonium-magnesium is apt to escape solution; (5) that varying percentages of phosphoric acid are dissolved when different weights of the same material are treated with a fixed amount of it; (6) that its action varies according as it is acid, neutral or alkaline,—Grupe and Tollens[2] recommend that a dilute (0.25 per cent.) solution of citric acid be employed in its stead. Like the citrate, it dissolves the tricalcium phosphate to a greater or less extent, according to its physical condition, but the authors apparently do not hope to find a reagent free from this objection. It dissolves the dicalcium and ammonium-magnesium phosphates with great ease, and vigorously attacks the phosphate of iron and aluminium. Its action is quite uniform, that is, a given amount of it will dissolve from two grams of material nearly the same percentage of phosphoric acid as from one. The phosphoric acid can be precipitated from it directly by molybdate, though this method is sometimes attended with a loss of 0.2–0.3 per cent. In order to obtain exact determinations of the phosphoric acid the authors recommend that the solution, whether citrate of ammonium or citric acid has been employed as the solvent, be evaporated with an excess of calcium oxide and the organic matter finally destroyed by heating the residue in a muffel. In this way a white ash is obtained without loss of material, and all the difficulties mentioned by Fresenius, Neubauer and Luck as attending the combustion with carbonate of sodium, saltpeter, etc., are avoided. H. N. MORSE.

[1] Versuchs-Stationen, **27**, 1, [2] Berichte der deutsch. chem. Gesellschaft, **14**, 754.

## Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra.[1]

In 1872 W. H. Hartley was led to these investigations by a desire to repeat and to carry out in a more complete manner the experiments of Miller, whose method of investigation and the results attained were published in 1863.[2] The end sought in this repetition of Miller's experiments was to find out what relation, if any, exists between the molecular constitution and the actinic absorption of organic substances. In his statement of results Miller says, "I have not been able to trace any special connection between the chemical complexity of a substance and its diactinic power"; so that very little inducement was offered to a continuance of these investigations. The difficulty of obtaining substances sufficiently pure for experiments of this nature is very great, and Dr. Hartley states that notwithstanding the extreme care taken in their purification, some of the substances examined by Miller were impure.

In 1872 (at which time Dr. Hartley and Prof. A. K. Huntington were associated in this work) Dr. Miller's apparatus was reconstructed and certain improvements were introduced. After some time spent in trying the various methods of studying the ultra-violet rays, the photographic method was selected as being decidedly the most satisfactory.

The instruments used were the following:

1st. An induction coil and Leyden jar for producing an unbroken stream of sparks between metal points. 2d. A collimator tube 3 feet long, carrying a pair of clips at one end for holding the points close to the slit, and a quartz lens at the other. 3d. A quartz prism placed at the angle of minimum deviation for the sodium line *D*. 4th. Another quartz lens, and the body of a photographic camera which could be extended to 36 inches. The fact that the lines of cadmium in the ultra-violet, as well as in the visible portion of the spectrum, have been measured and their wave-lengths calculated (by M. Mascart) has caused Hartley to adopt them as lines of reference in defining the position of absorption bands.

A complete description of the method of investigation and an account of some of the results reached by Hartley and Huntington were published in 1879.[3]

These results are summarized as follows:

1st. Every increment of $CH_2$ in a homologous series of alcohols and of acids effects an absorption of the more refrangible of the ultra-violet rays, so that the greater the number of carbon atoms in the molecule the shorter is the transmitted spectrum. 2d. Ter-

[1] Abstract of a paper in Journal Chem. Society, 1881, 153.
[2] Miller, On the Photographic Transparency of Various Bodies, etc., Phil. Trans. 1863, I.
[3] Phil. Trans. Part I, 1879.

penes with the composition $C_{10}H_{16}$ possess in a high degree the power of absorbing the ultra-violet rays of the spectrum, though they are inferior in this respect to benzene and its derivatives. Terpenes with the composition $C_{15}H_{24}$ have a greatly increased absorptive power, as shown by the greater extent to which they suffer dilution before the transmission of all rays is attained. 3d. Benzene and its derivatives, in addition to abnormally great absorptive power, show the peculiarity of *absorption bands* when dilute solutions are examined.

These results were attained by the examination of a very large number of substances of varied character. A consideration of the facts developed forced the investigators to the conclusion that *banded spectra* are caused by the compact molecular structure attributed by chemists to the double linking of three pairs of carbon atoms in a closed chain.

At this stage of the work the effect of various atomic groupings upon ultra-violet absorption was investigated. Ethylene, amylene, and allyl alcohol were examined, to ascertain whether bodies supposed to contain two adjacent carbon atoms doubly linked show any peculiarities in their absorption spectra. In the case of ethylene very little absorption was noticed. Carefully rectified amylene undiluted showed an absorption extending as far as the line *Cd* 17 wave-length = 274.34 (Mascart).

On diluting the liquid with pure alcohol to degrees varying between $\frac{1}{10}$th and $\frac{1}{1000}$th of the original volume, no intermediate absorption appeared. In the case of allyl alcohol no absorption bands were seen. A large number of isomeric alcohols, secondary and tertiary, were examined, but no absorption bands were noticed in any case.

To investigate the effect of the supposed treble linking of adjacent carbon atoms, acetylene was selected, being a substance easily prepared, and supposed moreover to be nearly related to benzene, on account of the ease with which it may be converted into the latter. An absorption extending to the line *Cd* 23 was revealed, but no absorption bands appeared. The experimenter's deduction from the examination of a large number of substances is, that "in all cases where the carbon atoms are supposed to be arranged in an open chain, no absorption bands are seen."

The occurrence of the absorption bands is in all cases independent of the arrangement of the hydrogen and oxygen atoms. No bands are caused by the replacement of hydrogen by various groups, such as $NH_2$, OH, etc., or by the halogens, when the result is a colorless body.

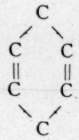
The next portion of the investigation is "*On the nature of actinic absorption exerted by various closed chains of carbon atoms.*"

With hydrocarbons containing at least six atoms of carbon, four arrangements of a symmetrical character are possible which admit of the carbon atoms forming a closed chain.

1st. Three pairs of carbon atoms may be doubly linked, as in Kekulé's formula for aromatic compounds generally.

2d. Each carbon atom may be directly combined with three other carbons, as in Ladenburg's prism formula.

3d. Two pairs of carbon atoms may be doubly linked, as is generally assumed to be the case in turpentine oil.



4th. The six carbon atoms may be singly united with each other, as in benzene hexachloride.

All substances which may be represented by either of the first two formulae show absorption bands in the spectra transmitted by dilute solutions. When the hydrogen atoms in benzene are replaced by alcohol radicals, or by the groups OH, $NH_2$, COOH or $NO_2$, bands still appear, but are modified first by a fusion of several narrow bands into one broad band, and second by an increase in the intensity of the absorption. The general conclusion here deduced is as follows:

"*The presence of absorption bands in the ultra-violet spectra transmitted by compounds of the aromatic series, is due to the particular arrangement of the six carbon atoms, forming the nucleus of the molecules of such compounds.*"

As an example of the third formula above given, turpentine oil was selected, and its examination revealed no absorption bands; the examination of about fifty essential oils showed that the terpenes when pure exert no selective absorption on the rays of the ultra violet spectrum.

Hence, assuming that terpenes have a nucleus in accordance with the third arrangement, it follows that: "*A closed chain of carbon atoms in which only two pairs of contiguous atoms are doubly linked, does not give rise to absorption bands.*"

As examples of compounds containing a closed chain of six atoms *singly linked*, camphor and camphoric acid were chosen. Various formulae for these substances have been proposed, namely

by Kekulé, Hlasiwetz, Kachler and Wreden. Kekulé's formula represents in each of these compounds a pair of adjacent carbon atoms *doubly linked;* the other three, however, agree in the point that there is a group or nucleus of six carbon atoms *singly linked;* all four agree in representing the nucleus as a closed chain. Solutions in alcohol of camphor and camphoric acid were prepared, varying between the limits $\frac{1}{70}$th and $\frac{1}{180}$th in the case of camphoric acid, and in the case of camphor to the minimum limit $\frac{1}{1000}$th. None of these solutions showed any absorption bands.

Benzene hexachloride is a typical example of a body containing six carbon atoms singly linked, and the examination of this substance was regarded as the crucial test of the correctness of previous deductions, the expectation in the case of this substance being, as also with camphor and camphoric acid, great freedom from absorption bands. The result of the examination of this substance proved the remarkable transparency of the substance and the entire absence of absorption bands.

Julius Thomsen has recently shown that the heat of combustion of benzene, if the carbons are linked as in Kekulé's formula, would amount to 846,040 heat units, whereas if there are nine single linkings in the molecule it would be 802,330 units. The experimental number obtained by Thomsen is 805,800; hence he concludes that the six carbon atoms in benzene are nine times singly linked with each other. Subject to the correctness of this deduction, the following conclusion is considered to be established:

"*No molecular arrangement of carbon atoms causes selective absorption unless each carbon is itself united to other three carbon atoms as in the case of benzene.*"

The investigation of naphthalene, anthracene and phenanthrene was then undertaken, with the expectation that the spectra of these substances would show a larger number of bands of greater intensity than appear in the spectrum of benzene. The constitution of naphthalene is generally represented by the fusion of two benzene nuclei, and that of anthracene and of phenanthrene by the fusion of three such nuclei. The anticipation was therefore natural, and was moreover to some extent satisfied by actual experiment. Dilutions in alcohol of naphthalene varying between $\frac{1}{1000}$th and $\frac{1}{100,000}$th of its weight, and in the case of anthracene and phenanthrene to the limits $\frac{1}{2000000}$th and $\frac{1}{20000000}$th of their weight of substance, were examined, and their spectra photographed.

In the hydrocarbons, benzene and the three just considered, the most prominent feature common to all the spectra is the group of four strong absorption bands, situated in the case of benzene in the most refrangible part of the spectrum, lowered in refrangibility in the case of naphthalene, and still further reduced in the cases of anthracene and phenanthrene.

In similar order the intensity of the absorption is increased, being at least forty times greater in the case of naphthalene than in benzene.

The next portion of the paper is: "*On the cause of absorption bands in the spectra transmitted by benzene and its derivatives.*"

In the absorption of the ultra-violet rays by hydrocarbons of the aromatic series we have two kinds of absorption manifested, namely a *general* absorption and a selective absorption. It is the selective absorption which distinguishes these from all other classes of carbon compounds. The absorptive power of alcohols and of fatty acids is dependent upon the number of carbon atoms in the molecule, while in aromatic compounds it depends entirely upon the *structure of the molecule.*

When a molecule of a substance is capable of vibrating synchronously with a radiation, the ray received on the substance is absorbed. The absorption is complete if the *direction* of vibration of the ray and of the molecule is the same, but the *phase* opposite. It is evident that general actinic absorption, exerted by carbon compounds, is due to the vibration of the molecules, since absorption increases in extent with the number of carbon atoms in the molecule; or, in other words, the larger the molecule the lower its rate of vibration. Selective absorption appears to be caused by the vibration of atoms within the molecule.

When a substance like benzene absorbs all rays beyond a certain refrangibility, it is because the molecules are vibrating synchronously with certain rays, and the number of molecules present is sufficient to damp all vibrations. When the liquid is diluted the number of molecules present is not sufficient to damp all the vibrations and some rays are transmitted. If, however, certain carbon atoms within the molecule are vibrating synchronously with certain rays, we shall have selective absorption of these rays after the general absorption has been so weakened by dilution as to allow them to pass.

The mean rate of vibration of the rays absorbed by naphthalene and anthracene is less than that of the rays absorbed by benzene. It follows from this that the bands in benzene, naphthalene and anthracene, though conceived to be caused by the vibration of the carbon atoms within the molecule, are not independent of, but are a consequence of the molecular vibrations; they must, in fact, be regarded as harmonics of the fundamental or molecular vibrations.

Musical instruments of the same construction, set in vibration in the same way, will always evolve tones of the same quality or wave form. Hence in the examination of molecular vibrations, as the same method of actuating the vibrations is always employed, the difference in wave-form must indicate a difference in structure, that is to say, in chemical constitution.

"It is easy to predict from this that as the wave-form must manifest itself in a variety of absorption bands, not only may substances be classified according to their transmitted spectra, but we may ascertain their chemical constitution; and if the bodies in question be isomerides, doubtless further research will enable us at once to determine whether they be ortho-, meta- or para-derivatives."

W. C. D.

# NOTES.

## *A New Gas-Regulator.*

The essential principles of this device are but little different from those of a great many others that have appeared within the last few years, and the writer claims for it no great amount of originality, except perhaps for the mechanical details of its construction, which he has endeavored to simplify as far as possible.

The construction of the regulator will be best understood by reference to the diagram. It consists essentially of three parts: a

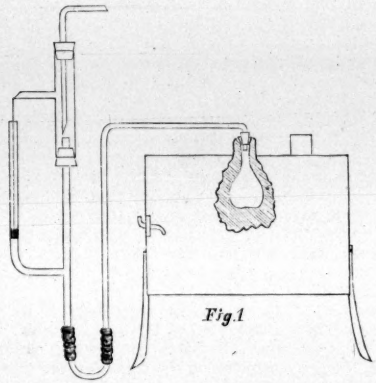


*Fig.1*

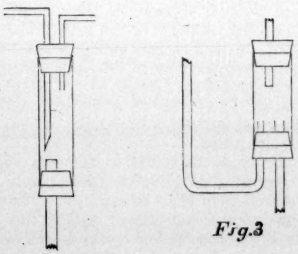


*Fig.3*

*Fig.2*

small glass flask used as an air chamber; a U tube, one limb of which is of rather small bore, while to the other, which is of larger tubing, is attached the apparatus for regulating the temperature; the tube through which the gas passes.

The air chamber may consist of flasks of different capacities, the larger ones for work at low temperatures, and the smaller ones for high temperatures. The lower end of the U tube is best made so that it may be attached to its limbs by means of pieces of rubber tubing, thus enabling us to lengthen the U tube when it is desired to increase the range of available temperature. The tube for the passage of the gas is similar to that in Bunsen's regulator, except that the inlet tube has its lower end beveled and is held in place by a rubber stopper. The desired temperature is attained by the use of the plunger in the small tube to the left. The plunger is made from a piece of very small glass tubing, a sole-leather disc of the proper size, a pin and some sealing-wax. If covered with some lubricating substance, such as water, glycerin, etc., it will be found to work much more easily.

The entire apparatus may be made without any glass-blowing beyond the mere bending of tubes, by the aid of the devices suggested in figs. 2 and 3.

To use the regulator, fill it with mercury until both limbs of the U tube are nearly full; if used with an air-bath, place the flask in the bath, as in the diagram, and by the use of the plunger produce the temperature desired, after which the instrument will automatically maintain this temperature for any length of time.

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## *Concerning the Halogens.*

In the course of the investigations of Victor Meyer on the specific gravity of chlorine at high temperatures, it was observed that in a number of experiments a small quantity of oxygen was obtained from the chlorine after it had been heated. These observations led to a careful examination of the subject, particularly with reference to the possibility of getting oxygen from chlorine. H. ZÜBLIN has just communicated the results of his studies. He found that, whenever a particular kind of porcelain—that from Bayeux—was used, oxygen was obtained; whereas, when vessels of platinum or of Berlin porcelain were used, no oxygen was obtained. By means of complicated and elaborate experiments it is proved that the oxygen obtained is a result of the action of the chlorine at high temperatures on the Bayeux porcelain. Attempts were made to separate the possible constituents of chlorine by diffusion. The diaphragms used were made of platinum, in which very fine holes were bored by means of a steel needle. No separation of chlorine into simpler bodies could be effected even at the

highest temperatures. Similar results were obtained with iodine and bromine. The paper concludes with this remark: "As the result of the work described, it may be stated that in spite of the most varied and the most favorable conditions for the separation of oxygen from the halogens, no observations were made which can in the least support the view that oxygen is contained in the halogens."—(*Annalen der Chemie*, **209**, 277.)

### *On the Synthetical Production of Urea from Benzene, Ammonia and Air by the Action of Heated Platinum.*

E. F. HERROUN describes some experiments undertaken by him as follows: "Air was drawn by means of an aspirator through washing bottles containing (1) ammonia and (2) benzene, the glass tubes conveying the air dipping below the surface of the liquid in both bottles, then through a tube containing a helix of platinum wire, heated to dull redness by a Bunsen burner, and finally through water contained in potash bulbs to absorb the products of the action.

"On analysis, the water at the end of the experiment was found to contain ammonium carbonate, nitrite, and nitrate; but it was also observed that a solid crystalline substance had collected in the tube containing the platinum, depositing not far from the heated wire. On analyzing this substance qualitatively it appeared to be ammonium cyanate, giving the following reactions: When treated with dilute sulphuric or hydrochloric acid it evolved cyanic acid, recognized by its odor. Its solution gave with silver nitrate a white precipitate, soluble in dilute nitric acid, and converted by hydrochloric acid into silver chloride, with evolution of cyanic acid. After boiling its aqueous solution and evaporating to a small bulk, it gave with strong nitric acid a crystalline precipitate, soluble in potash solution, and evolving ammonia when boiled with it, indicating its conversion into urea." Analysis showed that the substance finally obtained had the composition of urea.—(*Journal Chem. Soc.* 1881, 471.)

### *On Sewage in Oysters.*

C. A. CAMERON has lately examined oysters taken from the "beds" on the northern shore of the bay of Dublin, the water of which is yearly becoming more polluted with excrementitious and other offensive matters. The oysters were taken from a place where the tide covers them to a height of about ten feet, and which during low water is nearly dry. In most of the oysters the brine had no peculiar odor; but in a rather large proportion there was a very slight but distinctly foetid odor, whilst in a few cases there was a strong and unmistakable odor of sewage. Examined micro-

scopically, the liquid in the oysters which had a foetid odor was found to swarm with micrococci and other low organisms similar to those usually present in sewage. The water of the bay was examined at low tide, and it was found to be highly charged with sewage matter. Any one may satisfy himself that sewage is constantly discharging over fore-shores, in which various edible molluscs have their abiding-place; and it is in the highest degree improbable that animals can always resist successfully the entry of polluted brackish water into their calcareous dwellings. It may be that the illness which so many persons have experienced after eating oysters, believed to have been stale, was really due to the presence of sewage matter in the juice of the molluscs.—(*Chem. News*, **44**, 52.)

### *The Action of Compounds inimical to Bacterial Life.*

W. M. HAMLET has examined the behavior of bacteria when exposed to a variety of substances, including such as are classed as disinfectants and those which are poisonous to higher animals. The examination consisted in providing bacteria with the conditions necessary for growth, and noting the interruption to their normal development upon the addition of one or another substance. Beef tea, extract of meat, Pasteur's fluid, hay infusion, and other solutions capable of furnishing the required nourishment, were boiled to render them free from previously existing forms of life, and then impregnated with definite species of bacteria, usually *Bacteria termo* or *Monas crepusculum*. Small flasks were about half filled with these solutions and kept at a temperature of 25°C. The action of various gases was first determined.

Pure hydrogen was passed over the liquid in a flask. On examination at the end of three days the solution contained bacteria in abundance. Oxygen, carbon monoxide, marsh gas, nitrogen and sulphuretted hydrogen were likewise incapable of checking bacterial growth. Chlorine, nitric oxide and sulphur dioxide, on the other hand, left no trace of living bacteria in solutions through which they were passed. The addition of hydrogen peroxide was also fatal.

Various salts and organic acids were next experimented with, and the following compounds among others were found to have no decided effect when used in the form of five per cent. solutions, the bacteria developing readily in all of them: Potassium carbonate, ammonia, olive oil, castor oil, cod-liver oil, acid potassium sulphite, ammonium sulphate, acid potassium tartrate, benzoic acid, citric acid, oxalic acid, potassium iodide, potassium bromide, potassium permanganate, potassium chlorate, sodium hyposulphite, succinic acid, laudanum, potassium formate, tannin, acetic acid.

The following compounds were found to have effect upon bacteria, hindering their growth but not preventing their ultimate

development: Potassium and ammonia alums, ferrous sulphate, ferric chloride, magnesium and aluminium chlorides, bleaching powder, camphor, salicylic acid, chloroform, creosote and carbolic acid.

In these cases the bacteria became very sluggish in their movements. Another and more elaborate series of experiments with chloroform, creosote and carbolic acid only confirms the above result, and goes to show that bacteria may be kept in an inactive state for some time by the aid of the second class of compounds, but that they will proceed with their regular development when removed to favorable surroundings.

The author states that the best disinfecting agents are, in general, those capable of exerting an immediate and powerful oxidizing action, and that it is active oxygen, whether from the action of chlorine, nitric oxide or hydrogen peroxide, which must be regarded as the greatest known enemy to bacterial life.—(*Journal Chem. Soc.* 1881, 326.) D. T. D.

### *On a Suitable Reagent for distinguishing Ptomaïnes from Vegetable Alkaloids.*

Ptomaïnes, or alkaloids found in the human cadaver, present in general the most important chemical characteristics and physiological properties of the vegetable alkaloids, and may for that reason readily be mistaken for them. Such a mistake in fact occurred recently in Italy, the experts deciding that a certain individual had been poisoned by delphinine, when in reality the substance pronounced by them to be delphinine was found to be simply a ptomaïne resembling it. The rational way to distinguish in such a case between a ptomaïne and a vegetable alkaloid is evidently to determine all of the chemical and physiological properties of the suspected poison which has been isolated. If it is found to lack one or more of the known characteristics of the vegetable alkaloid, the presence of which seems to be indicated by other experiments, then the compound under examination is not that alkaloid, but probably a ptomaïne resembling it. This method, although the most sure, is inconvenient, and moreover can only be employed when the quantity of the suspected substance isolated is sufficient to allow of a complete study.

P. BROUARDEL and E. BOUTURY have devised a means of deciding the point, which is at the same time easy of application and reliable. Ferricyanide of potassium, when treated with a solution of a pure vegetable alkaloid, is unacted upon by it; while under the same conditions it is instantly reduced to the state of ferrocyanide by a ptomaïne and thus becomes capable of forming Prussian blue with a ferric salt. The method of applying the test is as follows: The base extracted from the cadaver, by the method

of Stas is converted into the sulphate, and a few drops of its solution placed in a watch-glass containing a few drops of solution of potassium ferricyanide. A drop of neutral ferric chloride added to this mixture produces a precipitate of Prussian blue, if the base isolated is a ptomaine, while no such effect is produced if it be a vegetable alkaloid. Up to the present but two exceptions to this general rule have been found—morphine, which readily reduces potassium ferricyanide, and veratrine, which gives traces of such reduction. It is possible, however, that in this last case the reducing action is due to certain impurities which the investigators were unable to completely remove from the veratrine employed by them.—(*Comptes rendus*, **92**, 1056.) R. D. C.

*On the Transformation of Morphine into Codeïne and Homologous Bases.*

The formula of morphine, $C_{17}H_{19}NO_3$, and that of codeïne, $C_{18}H_{21}NO_3$, show that these two bases differ from each other by $CH_2$, and that codeïne may be considered as derived from morphine by the substitution of a $CH_3$ group for one atom of hydrogen.. An English chemist, How, tried in 1853 the action of methyl iodide upon morphine, but he obtained an isomere of the hydriodate of codeïne, presenting none of the characteristics of an alkaloid salt. More recently Matthiessen and Wright have determined something of the relation of morphine to codeïne. By heating morphine with hydrochloric acid they extracted the elements of water, and obtained as a result apomorphine. Codeïne submitted to the same treatment likewise yielded apomorphine and also methyl chloride. There is therefore present in morphine an alcoholic OH group, and in codeïne a group $OCH_3$. In considering the various reactions of morphine it was observed by E. GRIMAUX that it resembled the phenols in its characteristics, and it occurred to him that codeïne might be the methyl ether of morphine considered as a phenol. It then only remained to try this transformation by the usual means, viz. heating with alcoholic potash or soda. Morphine was dissolved in alcoholic soda solution, the proportions being one molecule of morphine to one molecule of soda, and a quantity of methyl iodide corresponding to two molecules added. On gently heating the mixture brisk action took place, which ceased after a few minutes. The reaction took place in the manner expected, but was complicated by a secondary reaction, and in place of free codeïne there was obtained the iodomethylate of codeïne, $CH_3I.C_{17}H_{18}NO_2(OCH_3)$. At the same time that double decomposition took place between one molecule of the methyl iodide and the morphine, a second portion of the methyl iodide united directly with the molecule. The compound thus obtained was identical in every respect with the addition product of codeïne and methyl iodide.

On repeating the experiment, reducing the proportion of methyl iodide to half of that employed in the first operation, free codeïne was obtained; but the yield was very small,—20 grams of morphine yielding but 2 grams of hydrochlorate of codeïne. The codeïne thus obtained possessed the same crystalline form and all of the chemical characteristics of that extracted from opium, and was found to be in every respect absolutely identical with it. Upon operating with ethyl, in the place of methyl iodide, there was obtained a new base, $C_{19}H_{23}NO_3$, homologous with codeïne, which is the ethyl ether of morphine, considered as a phenol. This new base can be obtained in fine crystals, fusing at 83°, readily soluble in ether and alcohol, and a little less soluble than codeïne in boiling water. Its yield is from 40 to 45 per cent. of the weight of the morphine employed.

From morphine there can then be obtained a series of compounds of which codeïne is the type, a series numerically as great as the series of ethers from an alcohol. To this class of compounds M. Grimaux proposes to give the generic name of *codeïnes*, the codeïnes being the ethers of morphine. The methyl ether is *codomethyline*, or more simply codeïne, its homologue just described *codoethyline*, and so on. M. Grimaux announces his intention of preparing other compounds of this series, which appears to him to furnish an interesting subject of study to physiologists. —(*Comptes rendus*, **92**, 1140.) R. D. C.

### *Alleged Ozone as a Preservative.*

"Ozone" has been largely advertised within a few months as a new preservative for all kinds of animal and vegetable substances. The gas is produced by the combustion of a fine dark powder of cinnamon odor. This substance consists of sulphur mixed with a little carbonaceous matter. On burning, only 0.09 per cent. of ash remained.

These results are offered without waiting to complete the examination, because the so-called ozone is clearly shown to be sulphurous anhydride, whose destructive action on the germs of fermentation has long been well known.

R. B. WARDER.